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The commercial and economic progress of German industry has been a steady and prosperous one since last October, so that a retrospect at the close of the year offers a gratifying view. The only exceptions are some chemical establishments, whose annual account turned out to be less favorable. In consideration of the vast variety in the domain of chemical production, such comparatively few exceptions do not affect the general condition of industrial prosperity. The apprehension expressed in our recent Reports, in regard to an excessive production in some lines of chemical industry, particularly of medicinal synthetic novelties, seems to be verified by facts. Nevertheless, the general outlook for a steady progress of industrial and economic prosperity appears to be the more secure as the political position of the German empire remains undisturbed.

The export of products in our line of manufacture from Leipzig to the United States of America has experienced a considerable decline, as compared with the preceding year. This fact is evidenced by the figures of the last six months, and as yet no improvement is to be noticed.

### Export of essential Oils and Chemicals

from January 1<sup>st</sup> to December 31<sup>st</sup> 1897:

Jan. 1 <sup>st</sup> to March 31 <sup>st</sup> —	April 1 <sup>st</sup> to June 30 <sup>th</sup> —	July 1 <sup>st</sup> to Sept. 30 <sup>th</sup> —	Oct. 1 <sup>st</sup> to Dec. 31 <sup>st</sup>	Total
\$ 129,860.19	\$ 92,569.37	\$ 61,199.47	\$ 100,771.75	\$ 384,403.78

from January 1<sup>st</sup> to December 31<sup>st</sup> 1898:

Jan. 1 <sup>st</sup> to March 31 <sup>st</sup> —	April 1 <sup>st</sup> to June 30 <sup>th</sup> —	July 1 <sup>st</sup> to Sept. 30 <sup>th</sup> —	Oct. 1 <sup>st</sup> to Dec. 31 <sup>st</sup>	
\$ 78,254.08	\$ 72,972.31	\$ 66,444.99	\$ 83,495.—	\$ 301,166.38

Decrease \$ 83,237.40

Business in the United States remains slow and particularly dull in articles of luxury, while with all common goods of wholesale manufacture utmost price cutting prevails to a degree and extent unknown in Europe.

The commerce with Cuba has been more satisfactory. This island seems to recover from the effects of the late war more rapidly than was anticipated. For Cuba as well as for the Philippine Islands, the same regulations and formalities for the importation of merchandise are in force as in all ports in the United States.

The commercial and economic development of the Argentine Republic has been a prosperous one, as is evident from a perusal of the statistics of importation. A constant cause for irritation and warlike expenditures has fortunately been removed by the recent peaceful settlement of long standing boundary disputes with Chile. A favorable outlook is also reflected by the beneficial influence upon the paper currency values of the country.

Less propitious are the affairs of Chile, which apparently are in a somewhat critical state, notwithstanding the settlement of the boundary differences with the Argentine Republic. Scarcy of money is still prevailing. This reached a climax in consequence of the failure of the gold standard. It remains to be seen what the present paper currency will exercise upon the economic condition of the country.

Matters in Brazil are slowly improving without, however, excluding occasional disagreeable reverses to importers, like the tariff regulation, in operation since January 1<sup>st</sup> 1899, imposing payment in gold of 10 per cent of all import duties.

If the stock exchange quotations represent a correct criterion of the credit of a country, Spain seems to rally much more from the effects of a disastrous war than was expected. Valuations of credit have not been so favorable since quite a time.

In pursuance of a commercial treaty between France and Italy, the Italian government has reduced the duties on a number of products of French origin, a reduction of which Germany will also share the benefit, in consequence of the privileges to which it is entitled by the most favored nation clause in its treaties with Italy. This affects in our line of goods only rose oil, the duty for which has been reduced from £ 40.— to £ 20.— per kilo, and perhaps also perfumery devoid of alcohol, the duty on which has been reduced from £ 100.— to £ 50.— per kilo.

On the 1<sup>st</sup> of January of the present year, a new tariff has come into effect in Japan, inaugurating higher duties on all imported merchandise and replacing the old tariff, which had remained unchanged for thirty years. The new rates on products in our line amount on the average to 10 per cent. ad valorem, against 5 per cent. heretofore. In order to obtain the benefit of the reduction of rates granted by special treaties with the great powers, all shipments must be accompanied by certificates of origin. These papers must be certified by the Japanese consulate or authorised commercial agent. In places where no such officials are located, the certification of papers by the custom-house authorities or the officers of the Chamber of Commerce will be accepted as valid.

As is usual in the case of an impending increase of tariff duties, a very brisk business with Japanese ports was carried on

near the close of the year and many shipments arrived at the moment. It is a matter of course that very little import business is done during the first months of the present year.

The Trans-Siberian Rail-Road has been completed so far as to be worked from the boundary of Russia to Irkutsk in Siberia. It is said that the transportation of goods has already grown to such proportions that the Russian railroads connecting with the Siberian line are hardly able to promptly carry the mass of goods passing eastwards. It is not yet possible to foresee the vast changes in the commercial intercourse with Eastern Asia and Japan, which ultimately will result from the completion of this marvelous undertaking with its eastern terminus at Port Arthur and Wladiwostok.

The transactions in our line of products in general have been normal. Our efforts for diffusing an intelligent popular knowledge about the articles of our manufacture among the public are meeting more and more with appreciation and success in Germany and most European countries. We feel gratified by the unmistakable and ever increasing evidence of this fact.

In this connection it affords us a pleasure to announce the forthcoming publication of a comprehensive treatise on essential oils, elaborated at our initiative by well known scholars and experts. This work, the result of several years of labor, will not only be of great interest to the profession but not less to general readers, inasmuch as it treats the subject matter not only from its chemical, medical and commercial point of view, but also and more fully in its historical and practical aspects. Being a thoroughly modern work, it will also meet with approval by discarding the accumulated vast mass of antiquated and untenable literary material still prevailing in the current literature of essential oils. We feel justified in predicting that this work, to be published by the firm of Julius Springer in Berlin, in the course of this summer, will creditably fill a long standing void in this special domain of modern chemical literature.

The use of essential oils and artificial perfumes is constantly increasing and at the same time extending over new lines of application. Instances of such novel utilisation are the flavoring of fine writing and fancy papers, of textile materials, leather &c. used in the manufacture of articles of luxury; furthermore the flavoring of colors, candles, of sealing wax and similar commodities, making all such perfumed articles more pleasant and attractive to purchasers.

A prevailing abuse frequently misleading the public has recently been checked by a judicial decision rendered last December. This abuse consisted in marking goods "D. R. P. a." (Imperial German patent applied for), thereby conveying the false impression that this merchandise has secured, or is sure to obtain, patent rights. Henceforth this deception will be punished as a misdemeanor.

The researches and a closer study of the essential oils have continued to engage the interest and application of scientists and much work has been recorded during the last six months. The more important practical results of these investigations will be found briefly referred to in this Report, as also the commercial relations and changes of our principal products.

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**Allspice (Pimento) Oil.** The British pharmacopœia requires for this oil a specific gravity not below 1.040. The fact, however, is that there are oils in the market, otherwise of unobjectionable quality, whose specific gravity is 1.037 to 1.034 and a good oil of our own distillation had the specific gravity of only 1.024. As the statement of the British pharmacopœia requires a correction, we beg to call attention to this discrepancy.

**Almond Oil, bitter, natural.** The crop of apricot kernels, now almost exclusively used for obtaining this oil, has failed to reach the expected quantity. In consequence of this fact and of a brisk and persistent demand, prices reached higher rates than could be anticipated last fall. The disposal of the fat oil, on the other hand, has been a very limited one, so that the handling of this commodity has been altogether unprofitable this season. Several large orders of essential oil of bitter almonds could be effected only upon the condition of the additional order for a corresponding quantity of fat oil.

**Almond Oil, bitter, synthetic.** In consequence of an abundant production and favorable purchase of toluol, the price of common synthetic oil containing chlorine could be considerably reduced some months ago. The use of benzaldehyde in place of the disagreeable and poisonous nitrobenzol is fortunately increasing and is much preferable from a sanitary point of view.

**Almond Oil, fat, from sweet almonds.** Contrary to anticipation, the prices of sweet almonds have maintained their high rate at about *M.* 170.— per 100 kilos. As the stock has largely passed into the hands of the principal consumers there is no prospect for a reduction previous to the appearance of the new crop in the market. It is reported from Sicily that the flowerage of the almond trees has been an early and abundant one. This favorable aspect can, however, be altogether changed by a single night's frost.

As we obtain our oil by one single powerful hydraulic pressure only and on the largest scale, our product is of exceptionally good quality. The application of repeated pressure furnishes a greatly inferior oil. Our oil answers to the strictest pharmacopœial requirements.

**Angelica Oil.** The harvest of angelica roots, both in Thuringia and in Saxony has been a short one. In consequence, prices have

new raised and roots of good quality are scarce and much in demand. The same holds good for the small stock of oil left.

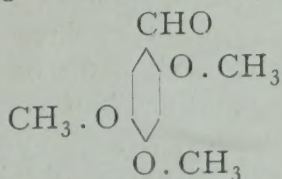
**Anise Oil.** The supply of Russian seed at reasonable rates has been abundant and the low prices of anise oil will continue the more since the Russian distillers supply large amounts of raw oil at cheap prices.

As repeatedly indicated in our former Reports, pure anethol, first manufactured by our firm, is more and more replacing anise oil, and justly so. Every intelligent consumer cannot fail to recognize the advantage of using anethol in place of anise oils. The price is only inconsiderably higher, but is counterbalanced by the greater intensity and moreover by the superior purity of the flavor. In regard to anise oil, the fact must also be taken into consideration that, in consequence of the depressed prices and the prevailing demand for cheap goods, common anise oil of the market is very variable in quality.

That the advantage of the use of anethol in place of the oil more and more recognized becomes patent from the fact that in our sphere of business the sale of anethol three times surpasses that of anise oil.

Our facilities for the manufacture of anethol have recently again been extended and perfected.

**Asarum Oil.** The constitution of the so-called asarum camphor which deposits in the oil upon refrigeration, to whose presence in matico oil we have called attention in our last Report<sup>1)</sup>, has not yet been fully elucidated. It was well known that it is an oxyhydrochinonetrimethylic ether wherein one atom of hydrogen of the aromatic nucleus has been replaced by a  $C_3H_5$ -group. It remained, however, uncertain where the substitution had taken place and whether the  $C_3H_5$ -group is an allyl or propenyl group. Eykman's<sup>2)</sup> investigation pointed towards the latter group. Prof. Gattermann, after having succeeded in effecting the synthesis of aromatic aldehydes, has in cooperation with Mr. F. Eggers, obtained asarylaldehyde by the incorporation of the aldehyde group into oxyhydrochinonetrimethylic ether. By heating asarylaldehyde with anhydric propionic acid and sodiumpropionate, asarone itself was obtained<sup>3)</sup>. At the latter reaction trimethoxymethylcinnamic acid is formed as an intermediate product, this yields asarone by elimination of carbonic acid. The constitution of oxyhydrochinone being known, that of asarylaldehyde must be



<sup>1)</sup> Schimmel & Co.'s Report, October 1898, p. 33.

<sup>2)</sup> Berichte der deutsch. chem. Ges. Vol. 22 (1889), p. 3172.

<sup>3)</sup> Ibidem vol. 32 (1899), p. 289.

since the agglomeration of the aldehyde group always takes place in the p-position to the oxalkyl group.

Asarone therefore is to be considered as being propenyltrimethoxybenzol  $C_6H_2C_3H_5^{[1]}.(O.CH_3)_3^{[2, 4, 5]}$ .

**Basilicum Oil.** We have left only 4 to 5 kilos of this exceedingly fine oil, much in favor for elegant mignonette perfumes. Larger orders cannot be filled before August.

**Boldo Oil,** distilled in Chile from the leaves of *Boldoa fragrans* Gay, is now offered in larger quantities. We have referred to this oil in our Reports of April 1888, p. 43, and of October 1890, p. 11 and after extended observation and upon re-investigation cannot but uphold our former estimate of this oil. On account of its disagreeable odor it is unfit for perfumery and for scenting toilet-soaps. Nor have the therapeutical properties claimed for the same been recognized by German practitioners. Boldo oil of our own distillation was included in our exhibit on the occasion of the 10<sup>th</sup> International Medical Congress at Berlin.

**Cajeput Oil.** In consequence of large speculative purchases this oil reached maximum prices in 1898. They have now declined from Fl. 2.15 to Fl. 1.40 per bottle. The supply was limited, amounting to about 4000 bottles which have so far been disposed of that only 600 bottles are remaining. The lowest price of this oil was Fl. 1.— per bottle in 1892, the highest one Fl. 2.70 in 1897. At such unusual rates, it is probable that frequently an admixture of eucalyptus oil has been practised, since this oil contains about the same percentage of cineol. In case the speculators at Makassar should continue this sort of bargain, they will ultimately hurt their own interests, inasmuch as in any shortcoming supply eucalyptus oil may fairly well replace cajeput oil.

The export of cajeput oil from Makassar amounted

in 1896	. . . . .	to 57,800 kilos
„ 1897	. . . . .	„ 78,543 „

The greater part of this is consumed in Asia, particularly in East India.

**Camphor Oil.** In consequence of the unusually high prices of oil of turpentine, attention has again been drawn to rectified light camphor oil. Although it cannot replace the former, yet it has proved to be a good solvent of all kinds of resins like colophony &c. and is still in vogue as a “perfume” of common soft soaps, so that it maintains its place in commerce and industry.

In the manufacture of safrol we obtain considerable quantities of the so-called heavy camphor oil of the sp. gr. of 0.970 at 15° C. and the boiling point of 240° to 300°. This oil has a light-green color and the consistency of a fat oil. It is perfectly non-poisonous,

not readily inflammable and acts like all essential oils, as a powerful disinfectant. The oil is also a good solvent of all sorts of resins, even of caoutchouc; it renders varnishes more elastic without retarding the process of drying. It has proved of special advantage as an addition to common colophony varnishes and is also well suited for concealing the strong odor of mineral oils, of carriage- and axle greases &c. without interfering in the least with the lubricity. It is also of great use in the manufacture of soaps, particularly of soft soaps and for checking the tallow-like or persistent odor of fats or oils extracted by means of benzine or carbon disulfide, like bone-oils. It is furthermore used for making greases of all kinds for leather, for hoofs, for boot-blackening &c.

The export of camphor oil from Japan has nearly been doubled in recent years, this being an evidence of its utility. It amounted to:—

1,094,910 catties . . . . .	in 1897
	against
558,859 „ . . . . .	„ 1896
516,792 „ . . . . .	„ 1895

The November number of the “Deutsches Handels - Archiv” of 1898 contains in a Consular Report for the year 1897 the statement that the number of camphor trees in Japan is constantly on the decrease and that a systematic replacing of the trees is nowhere carried on. It is also remarked that Japanese camphor, which used to be preferred to Formosa camphor, is becoming inferior, so that the latter more and more comes into favor in Europe.

The export of camphor from Japan amounted to:—

in 1898 to . . . . .	21,609 piculs
	against
„ 1897 „ . . . . .	24,084 „
„ 1896 „ . . . . .	15,565 „

**Cananga Oil.** According to Dutch statistics the following transactions in this commodity have taken place last year:—

In stock, January 1 <sup>st</sup> 1898 . . .	399 bottles
Import in 1898 . . . . .	783 „

Total: 1182 bottles,

which have all been sold at the old rates. Unsophisticated oil is rather scarce and great discrimination is necessary in the purchase of this oil, since much of questionable quality is in the market. Unfortunately there is no ready and reliable test for ascertaining the quality of the oil. The dealing in it, therefore, is entirely a matter of trust.

We have received from Messrs. Goethart & Co., pharmacists at Samarang, Java, two specimens of cananga oil, the one distilled

from green, the other from yellow flowers of *Cananga odorata* eth- constants obtained are:—

1. Oil from green flowers. Sp. gr. 0.930 at 15°; opt. rot. — 19° 21', number of saponification 24.31. Not soluble in 10 parts by volume of 95 percent. alcohol.
2. Oil from yellow flowers. Sp. gr. 0.956 at 15°; opt. rot. — 25° 11', at 18°. Insoluble in 10 parts by volume of 95 percent. alcohol.

The latter has a striking odor of eugenol. By agitating this oil with solution of sodium hydrate, 12 per cent. of this phenol were obtained. This could readily be converted into benzoyleugenol by the action of benzoic chloride. After the removal of the eugenol the oil had the following properties:—

Sp. gr. 0.929 at 15°; opt. rot. — 29° 45' at 17°; number of saponification 31.2. Insoluble in 10 parts by volume of 95 percent. alcohol.

Both oils are in their odor far inferior to the oils distilled at Manila.

**Caraway Oil.** Prices have remained unchanged on the whole, although the rates of the Dutch markets have recently been more steady and somewhat advancing. This rise of price is justified in consideration of the reduction of the remaining stock, but it is somewhat checked by lower offers on delivery of the prospective crop of 1899.

The generally well credited supplies from Norway have come into disfavor in the present season in consequence of a large admixture of, or entire substitution by, inferior Finland seeds. This grade is readily recognised by a smoky by-odor and taste and by an admixture of much light and whitish chaff.

According to a notice contained in the March number of the "Deutsches Handels-Archiv" of 1899, the importation of caraway seeds into Germany in 1897 is said to have amounted to:—

via Prussia per rail-way . . Fl. 507,302.—

„ Hamburg per shipping . . „ 418,856.—

Total: Fl. 926,158.—

corresponding to about 75,000 bales. The correctness of this statement seems, however, doubtful, inasmuch as this figure far surpasses the total amount of the crop of 1897.

**Cardamom Oil.** In consequence of the high prices of Ceylon cardamom the rates of its essential oil have been correspondingly raised. While the production of this spice is an inconsiderable one, the demand for the same, particularly in the honeycake (Lebkuchen) bakeries and for distilling, is a brisk one. The supply therefore, always meets with a prompt demand, and the price has risen from 2/6 to 3/9 per lb., or nearly *Rs* 9.— per kilo.

not reach the essential oils of other cardamom seeds are not salable in disinfection of their persistent camphoric by-odor. The principal even cardamom oil is for the manufacture of fine aromatic liquors.

We mentioned in our Report of April 1898 the considerable export of cardamom from Siam. Siam cardamom is not known in European commerce. Upon our inquiry the Imperial German Consul-General has favored us with the information that Siam cardamom is exclusively exported by Chinese dealers to China, where it commands a much higher price than in Europe, and also, that the production of cardamom in Siam is but a limited one.

**Cassia Oil.** The apprehension of a considerable rise of the prices of cassia oil in consequence of the disturbances prevailing in the province of Kwang-Si has proved fallacious. Just the reverse has taken place, a decline of values. The Hongkong market is fully supplied with all grades of oil and among them such as are rich in cinnamic aldehyde.

In general the trade in cassia oil has experienced a better consolidation, the oil being now estimated and bought exclusively by the amount of cinnamic aldehyde contained therein. The Hongkong dealers and exporters guarantee at all sales a definite percentage of aldehyde. This standard has met with universal acceptance in commerce and has restored the requisite confidence in this commodity.

We have not observed novel adulterants, for which the trade must always be on the lookout, and cannot but feel gratified by the success of our proceedings, which in interested and intelligent circles have everywhere met with appreciation and assent.

**Cassia Oil, synthetic.** By additional improvements in the manufacture of this product, we are enabled to regulate its price in compliance with that of the natural oil. Both oils are passing side by side because each is particularly adapted by special advantages for different applications. The synthetic oil, on account of its lighter color, is preferred for flavoring light-colored transparent soaps and also for confections, liquors &c. For these uses the oil must of course be perfectly free from chlorine.

The importance of this fine product may become specially noticeable and appreciated in case there should once happen a deficient supply of the natural oil. The certainty of having an excellent substitute always at disposal should maintain and increase the interest of consumers in this synthetic product.

For bottling and storing, aluminium containers have proved a success. They are now made absolutely tight.

**Celery Oil** distilled from the green leaves and exactly and strongly representing their aroma is meeting with so much favor, that we are obliged at least to double our celery plantations. The oil

is of special value to and mostly used by manufacturers of so and spice flavors, of aromatic vinegar and sauces, & mustard pickles &c. Since we have introduced this product into the market the demand for the oil obtained from the seed has almost entirely ceased. The reason for this fact becomes specially evident by comparing the flavor of celery-salt prepared with the one and the other oil.  $\frac{1}{4}$   $\frac{1}{2}$  Gm. of the oil of the leaves is sufficient to strongly impart the celery flavor to 1 kilo of salt. In using the oil the fact should be taken into consideration that each part by weight represents 1000 parts by weight of the fresh herb, or in other words 1 Gm. of oil is equivalent to 1 kilo of fresh herb.

At present we have sufficient stock on hand to meet any future demand. In consideration of the increasing favor which this aromatic finds, it seems doubtful whether our stock will suffice until new distillates can be obtained.

**Chione Oil.** The various species of *Chione* (Family *Rubiaceae*) are almost exclusively indigenous in the West-Indies; of these the best known species is *Chione glabra*, called "*Violette*" and *Palo blanco* on Porto Rico. The fresh wood and still more the bark of this tree have an aromatic somewhat fecal smell, which gradually disappears on exposure to the air. According to Messrs. Paul and Cownley<sup>1)</sup> the bark yields upon distillation with steam 1.5 per cent of a light-yellow oil, which is heavier than water and upon cooling to  $-20^{\circ}$  solidifies to a mass of acicular crystals. It exhibits the peculiar odor of the bark and has been investigated by Messrs. Dunstan and Henry<sup>2)</sup>. The oil consists mainly of a fluid constituent solidifying at a low temperature and boiling at about  $160^{\circ}$  under 34 Mm. pressure; it has the sp. gr.  $d_{40}^{150} = 0.850$  and the formula  $C_8H_8O_2$ . The odor of this constituent is exactly that of the oil; when it is acted upon by acetic anhydride, an acetic ester is formed, and by hydroxylamine and phenylhydrazine compounds result which admit the inference that a carbonyl group is present. When fused with an excess of potash, salicylic acid and as a product of further decomposition phenol is obtained. When treated with nitric acid, picric acid is formed. All these reactions indicate that the chief constituent is o-oxyacetophenone  $C_6H_4 \cdot OH^{[2]} \cdot CO \cdot CH_3^{[1]}$ . A compound obtained synthetically from o-nitrocinnamic acid proved to be identical with that isolated from the oil.

Besides this compound  $C_8H_8O_2$ , the oil contains another colorless and crystalline substance, melting at  $82^{\circ}$ , which perhaps may be an alkyl derivative of the former. On account of its small quantity, it could not be more closely investigated. The volatile oil furthermore contains traces of nitrogenous constituents, but the authors could not

<sup>1)</sup> Pharmaz. Journ. (London) IV. 7 (1898), 51.

obtain evidence of the presence of indol or prepare derivatives thereof, although the odor of the raw material points to their presence.

**Cinnamon Oil, Ceylon.** The cinnamon market has settled down somewhat during recent months, but the prices still remain high. The transactions in cinnamon chips, the material used for the distillation of the oil, have surpassed any former ones. In 1898: 1,414,165 lbs. have been shipped, against 1,067,051 in 1897. These consignments went to:

Germany . . . . .	442,716 lbs.
England . . . . .	402,385 „
America . . . . .	144,816 „
Austria . . . . .	123,704 „
Italy . . . . .	120,960 „
Belgium . . . . .	62,376 „
France . . . . .	60,536 „
Holland . . . . .	22,400 „
Spain . . . . .	16,800 „
Australia . . . . .	17,360 „
Turkey . . . . .	112 „

Total: 1,414,165 lbs.

The chips reached the highest price at 4 d. per lb., and since several months have brought  $3\frac{1}{4}$  to  $3\frac{1}{2}$  d. per lb. at Hamburg. The above figures show that Germany is now ranging at the head in the consumption of this commodity. Ceylon-cinnamon oil is a specialty of our firm.

**Citronella Oil.** The transactions in this article have again considerably increased in 1898. The export from Colombo and Galle (Ceylon) reached the as yet greatest maximum figure, namely 1,365,917 lbs., consigned to the following countries:—

England . . . . .	696,869 lbs.
America . . . . .	618,999 „
Germany . . . . .	22,883 „
Australia . . . . .	10,633 „
India . . . . .	10,100 „
France . . . . .	3,440 „
China . . . . .	2,249 „
Singapore . . . . .	504 „
Africa . . . . .	240 „

Total: 1,365,917 lbs.

These figures, however, do not exactly indicate the real consuming countries, for a considerable part of the oil destined for Germany and France only passes through England in transit. In our estimate Germany consumes at least 220,000 lbs., or about one sixth of the entire production.

A recent paper on the production of citronella oil, published in the October number (1898) of the "Tropical Agriculturist", agrees in the principle points with the information given in our Report of October 1898. Two kinds of citronella grass, "*Maha pangiri*" and "*Lenabatu pangiri*" are said to serve for distillation. The former is hardly cultivated any longer, while the latter was little known 25 years ago. *Maha pangiri* is said to be richer in oil but to require after a cultivation for 10 to 15 years.

The cultivation of citronella grass and the distillation of the oil are now sufficiently well known so that every one interested in them can readily obtain all desired information. The well known simple and reliable method of testing the oil, elaborated by us and called "Schimmel's test", meets with approval and success. The proper rejoinder to some objections raised against it may be found on pages 16 and 17 of our October Report of 1898. Our test is in every respect as reliable as it is practical and deserving of full confidence and general application.

A first shipment of citronella oil from a new plantation and distillery from Java, amounting to about 300 kilos, is on its way to us. Preliminary specimens which have reached us indicate an oil of superior quality of a very light color and high percentage of geraniol. We must, however, defer our final estimate until the arrival of the gross lot.

According to a recent statement in No. 986 of the "Chemist and Druggist" (London), a syndicate of Arabs has purchased a considerable area in Queensland for the purpose of raising citronella grass for distillation.

**Clove Oil.** The trade in Zanzibar cloves is undergoing a change which possibly may lead to a displacement of the London market from its position as the principal distributing centre of this commodity. Term markets for cloves have been instituted at Amsterdam and at Rotterdam with a view of directing and concentrating the clove market in Holland. As an initial step towards this transference 10,000 bales of cloves are said to have been purchased in different markets to be laid in store in Holland. To all appearances the Dutch do not intend directly to enter upon a bona fide importation, but to engage in the principal transactions in and control of, the jobbing trade. Such a turn, however, would be an unfavorable one, inasmuch as there is no valid cause for establishing a term market for cloves and as the value of the article very likely would be subjected to wanton speculation. It is therefore to be expected that the venture will not meet with favor or encouragement, nor will the local firms in Hamburg and London having branches and deposits in Zanzibar readily relinquish their strong position.

The reports on the recent clove crop in Zanzibar and Pemba are

set with distrust and it is generally admitted that the yield will amount to about 100,000 gonjes, equal to about 6,000,000 kilos. The cry of a scarcity of manual labor for plucking the cloves in consequence of the abolition of slavery seems to be a hoax, again confirming the fact that credence should not be given to every vague report from transoceanic colonies.

The price of cloves is a reasonable and normal one at present that there is no risk in engaging upon larger sales. The distillation of all grades of oil of cloves on the largest scale is a specialty of our establishments both in Leipzig and New-York.

**Cochlearia Oil.** In consequence of the scanty yield of the green flowering herb and the corresponding high price of this oil, the synthetic isobutyl-mustard oil is substituted for most practical uses.<sup>1)</sup> Although we are well aware of the fact that this product can not serve as a perfect substitute of cochlearia oil, it certainly does deserve the preference over allyl-mustard oil or mixtures of the same with other oils.

Mr. J. Gadamer, to whom we owe several interesting researches on the constituents of the various mustard seeds as well as on the formation of mustard oils, has observed that the dried herb of *cochlearia* without flowers, after having been soaked in water together with some powdered white mustard seed, furnishes a considerably higher yield — 0.236 per cent. — of essential oil. The oil contains, as has been ascertained by the late Professor A. W. von Hofmann, as principal constituent secondary butyl-mustard oil,  $\text{SCN} \cdot \text{CH} < \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C} \text{H}_3 \end{smallmatrix}$ , but no isobutyl-mustard oil. It has the specific gravity  $d_{20} = 0.94179$  and the refractive index  $n_{D20} = 1.4932$ ; at a temperature of  $150^\circ$  to  $162^\circ$  it distills, leaving a small residue (perhaps 5 per cent). As the formula of the secondary butyl-mustard oil contains an asymmetric carbon atom, the inference must be drawn that the oil is optically active. The fact is that the unrectified oil showed a dextrorotation of  $(\alpha)_D + 55^\circ 27'$ . The secondary butylthiourea, originating by the action of ammonia upon the oil, is also optically active. All efforts to obtain therefrom the optically active secondary butylamine have failed, yielding in every case the inactive amine only. When cochlearia oil is heated to  $200^\circ$  for some time with water in a closed tube, besides inactive secondary butylamine, dibutylthiourea,  $\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_4\text{H}_9$ , melting at  $108^\circ$  to  $110^\circ$ , is formed, evidently by the action of the amine upon mustard oil.

**Cognac Oil** (Oil of Wine Yeast). Little has as yet become known about the properties of this oil and in order to obtain a better knowledge about it, we have distilled cognac oil from wine yeast obtained from the vineyards of the Rhine district, as well as

<sup>1)</sup> See our Report, October 1894, p. 18.

from Lausatia. The results are presented in the following table which we have added the constants observed with German, Spanish and with synthetic cognac oil for comparison.

Origine	Spec. grav. at 15°	Opt. rot. at 20°	Acidity number	Ester number	Solubility
From the Rhine Raw oil from wine yeast	0.878	— 0° 3'	55.2	207.3	{ sol. in 2 vol. and m <sup>l</sup> 80 percent. alcohol
The same recti- fied	0.879	— 0° 4'	50.9	218.6	do.
From Lausatia Raw oil from wine yeast	0.880	— 0° 10'	70.9	210.8	do.
The same recti- fied	0.880	— 0° 11'	68.6	140.9	do.
Spanish . . . .	0.876	—	37.1	212.4	{ insol. in 80 perc. alco <sup>h</sup> sol. in 1/2 vol. and m <sup>l</sup> 90 percent. alcohol
Commercial .	0.883	+ 0° 43'	105.5	172.8	{ sol. in 2 vol. and m <sup>l</sup> 80 percent. alcohol
Synthetic . . .	0.871	+ 0°	5.8	291.7	{ sol. in 10 vol. and more 70 percent. alcohol

In consideration of the as yet insufficient analytical evidence a definite standard for the purity of cognac oil cannot be advanced. So much, however, seems to be certain that a very low specific gravity and a high percentage of ester indicate the presence of artificial cognac oil.

**Coriander Oil.** A great change has occurred in the commercial relations and prices of this commodity since the last harvest. The fruit used to be imported from Russia to Germany in considerable quantities. Since the last season this supply has been altogether discontinued and the coriander has been distilled in Russia and the oil brought into the markets. Great expectations are evidently placed by the Russian producers upon this venture. They, however, leave the fact out of consideration that the cultivation of coriander is remaining a considerable one in Thuringia, and that the aroma of Thuringian oil of coriander is a superior one.

**Cubeb Oil.** The interest in and use of this oil is more and more vanishing. Under these circumstances the value of the drug is correspondingly low. In 1898 2414 piculs or 4000 bales were shipped from Singapore to America and but 393 bales to Holland where 1250 bales remained in public store at the end of the year.

**Cypress Oil.** The use of this oil as an efficient relief from the sufferings caused by whooping-cough (*pertussis*) is more and more recognized and appreciated; in consequence, its demand for medi-

oil use is already a regular one. It never fails to promptly afford relief and in most cases assists in or secures a cure.

### Essential Oils, Sicilian and Calabrian.

The following statistical compilation bears evidence to the fact, that the exportation of these essences fell considerably short of that of the preceding year. That their prices, nevertheless, maintained a rate above that of the year 1897, is a conclusive proof that the production of essences during the season 1897 to 1898 has been a smaller one than that of the preceding season. The fact is that we had to enter the last season without any stock of essences left on hand. This accounts for the high prices prevailing during the last six months of 1898, as well as for the higher quotations at the beginning of the present season.

Dealers and speculators abroad deferred their purchases during the months preceding the new manufacturing season in the expectation of having the benefit of cheaper rates at the incoming of the new crop; but when it turned out that new essences were at first scarce and hard to obtain, they were forced, in order to meet the demand, to purchase though it be at a loss, with the consequence that prices gradually rose. The incoming supply of new essences fell short of the demand. This is to be seen from the following figures:—

Months	Export during the season :	
	1897/98	1898/99
November . . .	30,610 kilos	40,824 kilos
December . . .	22,779 „	85,541 „
January . . .	78,797 „	84,176 „
February . . .	57,193 „	68,166 „

189,379 kilos against 278,707 kilos.

The export during the months of November 1898 to February 1899 exceeded that during the same time of the preceding year by 89,328 kilos.

An additional drawback consisted in the high prices and a scarcity of copper which is used for the manufacture of the containers. The delay resulting therefrom is the cause that all importers are still behind time in their shipments and that a buoyant tendency in prices prevailed until some accumulation of stock had taken place.

For the following customary statistical tables we are again indebted to the favor of the Imperial German Consul at Messina, Mr. Eduardo Jacob.

## Export of essential oils.

a) from Messina.

	1897		1898	
	Quantity kilos	Value Lire	Quantity kilos	Value Lire
North German ports . . . . .	16,877	227,839	16,884	219,490
Austria . . . . .	53,776	725,976	48,737	633,580
Belgium . . . . .	2,000	27,000	2,210	28,730
Denmark . . . . .	4,838	65,313	3,878	50,414
France . . . . .	35,851	483,989	41,389	538,057
United Kingdom . . . . .	221,521	2,990,534	191,431	2,488,603
Holland . . . . .	6,166	83,241	8,018	104,234
Russia . . . . .	4,987	67,325	5,650	73,450
Scandinavia . . . . .	2,226	30,051	1,460	18,980
Spain and Portugal . . . . .	2,152	29,052	965	12,545
Turkey . . . . .	725	9,788	744	9,672
North America . . . . .	189,319	2,555,806	183,611	2,386,943
South America . . . . .	3,639	49,127	1,235	16,055
Australia . . . . .	10,539	142,276	13,765	178,945
Egypt . . . . .	4,160	56,160	2,826	36,738
Greece . . . . .	402	5,427	271	3,523
India . . . . .	923	12,460	700	9,100
Malta . . . . .	402	6,237	325	4,225
Other countries . . . . .	225	3,017	—	—
Total	560,788	7,570,618	524,099	6,813,287

b) from Reggio.

Austria . . . . .	27,719	415,785	26,853	456,501
France . . . . .	23,982	359,730	18,121	308,057
North German ports . . . . .	2,156	32,340	2,376	40,390
United Kingdom . . . . .	2,200	33,000	7,996	135,932
Denmark . . . . .	400	6,000	140	2,380
Scandinavia . . . . .	—	—	571	9,707
North America . . . . .	30,483	457,245	28,658	487,186
Other countries . . . . .	155	2,325	354	6,018
Total	87,095	1,306,425	85,069	1,446,171

c) from Catania.

Austria . . . . .	4,716	47,160	2,201	28,613
France . . . . .	—	—	—	—
United Kingdom . . . . .	3,018	30,180	4,115	53,495
North German ports . . . . .	400	4,000	50	650
North America . . . . .	3,322	33,220	—	—
Holland . . . . .	560	5,600	—	—
Total	12,016	120,160	6,366	82,758

d) from Palermo.

	1897		1898	
	Quantity kilos	Value Lire	Quantity kilos	Value Lire
Austria . . . . .	5,150	51,500	9,610	124,930
North German ports . .	520	5,200	380	4,940
France . . . . .	29	290	530	6,890
United Kingdom . . .	41,754	417,540	36,180	470,340
North America . . . .	23,980	239,800	4,511	58,643
Other countries . . .	760	7,600	548	7,124
Total	72,193	721,930	51,759	672,867

Recapitulation.

1897.

Exports from Messina . . . . kilos	560,788	value Lire	7,570,618
„ „ Reggio . . . . „	87,095	„ „	1,306,425
„ „ Catania . . . . „	12,016	„ „	120,160
„ „ Palermo . . . . „	72,193	„ „	721,930

Total amount of exports in 1897 kilos 732,092 value Lire 9,719,133

1898.

Exports from Messina . . . . kilos	524,099	value Lire	6,813,287
„ „ Reggio . . . . „	85,069	„ „	1,446,171
„ „ Catania . . . . „	6,366	„ „	82,758
„ „ Palermo . . . . „	51,759	„ „	672,867

Total amount of exports in 1898 kilos 667,293 value Lire 9,015,083

1897: kilos 732,092 value Lire 9,719,133

1898: „ 667,293 „ „ 9,015,083

less in 1898: kilos 64,799 value Lire 704,050

The export of essences during the last 10 years amounted to:

in 1889 . . kilos	277,599	value Lire	4,206,258.—
„ 1890 . . „	301,879	„ „	5,056,214.—
„ 1891 . . „	264,150	„ „	4,954,655.—
„ 1892 . . „	359,378	„ „	5,543,358.—
„ 1893 . . „	588,334	„ „	9,356,814.—
„ 1894 . . „	666,740	„ „	8,308,148.—
„ 1895 . . „	554,191	„ „	8,081,870.—
„ 1896 . . „	514,067	„ „	7,579,424.—
„ 1897 . . „	732,092	„ „	9,719,133.—
„ 1898 . . „	667,293	„ „	9,015,083.—

**Bergamot Oil.** The yield of bergamot oil has been both quantitatively and qualitatively unsatisfactory at the recent crop, and the anticipations expressed in our last Report, we are sorry to say, have proved correct. Although the difference between the two last crops has been somewhat lessened by a larger yield of oil of the present fruit crop, the total production of oil has hardly reached 80 per cent. of last year's production. But of much more disadvantage is the fact, that in consequence of the abnormal weather of last summer the amount of linalyl acetate contained in the oil is considerably less (by 3 to 4 per cent.) than that of last year. High grade oils are scarce and their relatively high prices will prevail until the next crop.

The average amount of ester of this year's oil is 34 to 35 per cent. In consequence of this shortcoming, the old oil far richer in ester was used as long as the containers yielded a supply, and not before were new purchases entered upon. This fact again had the result that the inferiority of the new crop came to be felt rather late. If the prices nevertheless somewhat rose at first, this proves that higher rates would have been justified, if it had not been for the inferiority of the new oil.

It was specially difficult to attain to an approximately correct estimate of the total quantity of oil turned out this year; 35,000 to 40,000 kilos may be near the truth, while the total stock on hand may amount to about 15,000 kilos. Until the new crop comes in, the prices will entirely depend upon the greater or smaller demand. At the time this is slow and dull.

**Lemon Oil.** As anticipated in our last Report, the lemon crop of 1898/99 has about equalled that of last year. The demand and the prices abroad were so favorable that large quantities of the fruits, otherwise used for the manufacture of oil, went abroad. This circumstance, favorable for the producers but less so for the manufacturers, caused a delay in the production of oil and a higher price of the remaining fruits. Meanwhile the demand for fresh oil increased and the price rose by about *M* 1.— per kilo, but soon suffered a reduction when it became evident that the foreign markets were fully supplied.

An additional factor maintaining comparatively high rates consisted in the demand for concentrated lemon juice and calcium citrate, both rising in price by 30 to 40 per cent. during January; this rise of course reacted upon the value of the fresh lemon juice too.

The manufacturer of lemon oil, therefore, realized a good price for the oil and a still better one for the juice of the fruit, and the production of oil would have been a much larger one if it had not been for the brisk demand for and export of, the fruits. Nevertheless it cannot be denied that more lemon oil was manufactured during the last two months than was to be expected.

The manufacturing season is approaching its end, except at

The stock presently at hand in Messina may amount to 55,000 to 60,000 kilos. The prices, however, have suffered such a decline during the last weeks that a further reduction seems to be excluded. The time for laying in fresh stock therefore seems to be favorable.

It may be mentioned here that the lemon oil of the present crop shows a considerable decrease of its rotatory power, which is nearly  $4^{\circ}$  lower than that of the oil of the preceding year. It is difficult to find lots of lemon oil having an average rotation of  $60^{\circ}$ . Otherwise the quality and particularly the flavor of the new oil are excellent.

It may also be of interest to call attention to the efforts made by interested manufacturers and land owners to form a combine for monopolizing the by-products of the lemon trade, essences and juice. Although these efforts have proved a failure, the idea of their final realisation has not been abandoned and it is not unlikely that in the future the manufacture of lemon oil may have to confront such combines or trusts.

A more serious drawback for the future of the lemon oil trade is the mischievous tendency to manufacture so-called extra strong essences. The number of establishments supplying the foreign markets with oil sophisticated with citrene and other by-products of the foresaid manufacture in place of the natural oil is constantly increasing. It is greatly to be desired that a practical and reliable method may be found for detecting this kind of adulteration. The difficulties in the way have been pointed out in our former Reports.

No exact predictions can be advanced in regard to next year's crop. The last winter was short in rain, whereby the vitality of the trees is generally somewhat impaired.

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Messrs. Umney and Swinton have verified their former statement<sup>1)</sup> that geranyl acetate forms a constituent of lemon oil.<sup>2)</sup> By distillation under reduced pressure they separated 90 per cent. from 2 kilos of Messina lemon oil; the remaining 10 per cent. were repeatedly agitated with a warm 30 per cent. solution of sodium bisulfite until the oil did not show any further decrease of volume. The washed and dried oil, containing 35.7 per cent. of ester (calculated for geranyl acetate), was saponified and the alkaline saponification liquor evaporated. By distillation of the remainder with dilute sulfuric acid, acetic acid was separated and analyzed by converting it into acetate of silver. For the identification of alcohols present, a larger quantity of lemon oil was employed for these experiments. The alcoholic constituents isolated as described rendered, at  $225^{\circ}$  to  $240^{\circ}$ , a fraction having the sp. gr.  $d_{15} = 0.887$  and the opt. rot.  $+5^{\circ}$ .

<sup>1)</sup> See our Report, October 1898, p. 23.

<sup>2)</sup> London. Pharm. Journ. 61 (1898), II, 370.

The authors obtained therefrom by repeated fractionation and by treatment with chloride of calcium pure geraniol, whose identity was proved by oxidation to citral.

They also found in the same way the presence of linalool ( $d = 0.876$ ;  $\alpha_D = -16^\circ$ ) and of geraniol in Palermo lemon oil; evidence of the latter compound could be obtained less readily and only by the aid of the calcium chloride compound. Citronellol, supposed to be present, because citronellal is a constituent of both Messina and Palermo oils, could not be found.

**Orange Oil, sweet.** The orange crop has been an abundant one. The growers maintained high prices, thereby somewhat delaying the sales until it became evident that the fruits were not durable enough to be boxed and shipped to any distance. In consequence, the manufacturers had the benefit of an ample supply but this was greatly invalidated, since the peels of the oranges by long standing had lost much of their oil and in fact had become unprofitable for obtaining oil.

In order to turn the fruits to account, immense quantities were sent by rail to the Northern Italian markets and disposed of at low rates.

As the stock left from the preceding year was a short one, the new oil met with brisk demand for several months and prices were buoyant for some time, but soon relapsed in consequence of the general dullness of business.

The quantity of oil produced in Sicily in the present season is estimated at 27,000 to 30,000 kilos, and the old stock still on hand at 8000 kilos.

Mr. J. Parry<sup>1</sup>) has recently published a note on the oil of the Tangerine oranges, which somewhat differs from the ordinary oils of sweet and bitter oranges. An unquestionably genuine and pure specimen had the specific gravity  $d_{15.5^\circ} = 0.8589$  and the rotatory power  $(\alpha)_D = +70^\circ 47'$ . These figures are nearly coincident with those of Mandarin oil ( $d_{15^\circ} = 0.854$  to  $0.858$ ;  $(\alpha)_D = +65^\circ$  to  $75^\circ$ ). Upon considerable cooling, some fine needle-shaped yellow crystals separated; when recrystallized from their solution in alcohol, they retained their color and melted at about  $70^\circ$ . They probably correspond to the limettine obtained from limetta oil.

**Estragon Oil.** We are able to supply this specialty of our Miltitz establishment in an exceptionally fine quality and at comparatively low rates. For the supply of the herb we are now entirely independent of foreign countries. 250 Gm. of oil represent 100 kilos of the fresh herb.

<sup>1</sup>) The Chemist and Druggist 53 (1899, I), 420.

**Eucalyptus Oil.** The demand for this oil during recent months has been enormous. The oil seems to have come into popular domestic use in Germany and great quantities are lately used abroad for the manufacture of medicinal soaps. Sufficient supplies from Africa have restored any deficiency and 6000 lbs. more are on the way for us from Australia via London. In consequence of the increased demand higher prices for the oil may be anticipated.

The various eucalyptus oils have always been grouped into two classes, namely those with a high percentage of eucalyptol (cineol), obtained mainly from *Eucalyptus globulus*, and those containing phellandrene, mostly distillates from *Eucalyptus amygdalina*. In the belief that for medical purposes eucalyptol is the efficient factor, the former group of oil has been employed exclusively for medical preparations and application. This is in accord with the new English pharmacopœia, which recognizes only the distillate from *Eucalyptus globulus*.

According to a statement of Messrs. Baker and Smith<sup>1)</sup> several species of *Eucalyptus* are known in New South Wales by the name of "Stringybark Trees"; these are *Eucalyptus obliqua* L'Hér., *E. Baileyana* F. v. M., *E. macrorrhyncha* F. v. M., *E. capitellata* Sm., *E. eugenioides* Sieb., and *E. fastigiata* Deane and Maiden, to which may be added *Eucalyptus piperita* Link and *E. triantha* Link. The best known of these "Stringybarks" namely *Eucalyptus macrorrhyncha* (red Stringybark), *E. capitellata* (white Stringybark) and *E. eugenioides* (brown Stringybark) have been studied in their botanical relations by Messrs. Deane and Maiden<sup>2)</sup>. About the oils obtained from these species Messrs. Baker and Smith have published the following notes:

**Oil of *Eucalyptus macrorrhyncha*.** The average yield obtained from nine distillations amounted to 0.287 per cent.; the oil has a reddish-brown color and an agreeable odor; its specific gravity is  $d_{180} = 0.927$ . On account of its dark color the optical rotation could not be determined, it seems however to be a varying one, inasmuch as both a dextrogyrate and a laevogyrate rotation were observed with fractions with a low boiling point. The raw oil did not render a strong reaction of cineol with phosphoric acid, but from the fraction distilled at  $177.6^{\circ}$  to  $180^{\circ}$  a percentage of 53.2 of cineol could be obtained. The oil also contains traces of phellandrene and of ester-like constituents. The fractions with high boiling points gradually solidify and contain much "Eudesmol"<sup>3)</sup>.

<sup>1)</sup> On the "Stringybark Trees" of New South Wales, especially in regard to their essential oils. Proc. of the Royal Soc. of N. S. Wales 32 (1898), 104.

<sup>2)</sup> Proc. Linn. Soc. of N. S. Wales 21 (1896), 798.

<sup>3)</sup> This substance was first obtained by the authors from the oil of *Eucalyptus piperita* Sm. ("Sydney Peppermint"). It is said to melt at  $74^{\circ}$  to  $75^{\circ}$  and to boil at  $270^{\circ}$  to  $272^{\circ}$ . (Proc. Royal Soc. N. S. Wales 31 (1897), 198.)

**Oil of *Eucalyptus capitellata*.** The raw oil (yield 0.103 per cent) has the specific gravity  $d_{180} = 0.9153$ ; on account of its dark color the optical rotation could not be ascertained. The fraction distilling between  $174.5^{\circ}$  and  $198.2^{\circ}$  yielded 38.4 per cent. of cineol. The oil contains traces of phellandrene and only little "Eudesmol".

**Oil of *Eucalyptus eugenioïdes*.** Yield 0.689 to 0.795 per cent. The oil is almost colorless and has an agreeable odor, the specific gravity  $d_{220} = 0.907$  to  $0.908$  and the rotatory power  $(\alpha)_D = +3.745^{\circ}$  to  $+5.246^{\circ}$ . With two samples the percentage of eucalyptol proved to amount to 28.1 and 31.4; phellandrene could not be found in the oil.

The authors feel justified to call attention to and to predict a useful application of the oil of *Eucalyptus macrorrhyncha*.

In connection with this subject-matter a brief report on two other eucalyptus species of N. S. Wales recently described by Mr. R. T. Baker<sup>1)</sup> may be added; these are *E. laevopinea* ("Silver-Top Stringybark") and *E. dextropinea* ("Messmate" or "Stringybark"). The oils obtained from these species have been examined by Mr. G. Smith<sup>2)</sup>. They are of interest in that they mainly consist of pinene, a hydrocarbon as yet found only in small quantities in the oils of the group of *E. globulus*. On the other hand they contain very little cineol, the presence of which could be determined by the jodol and bromide of hydrogen reaction. It remains to be seen by further observations whether the amount of cineol in both oils at the various seasons is a constant one.

Mr. Smith states that *E. dextropinea* yields 0.825 to 0.850 per cent. of oil, having the specific gravity  $d_{170} = 0.8743$  to  $0.8763$ , and *E. laevopinea* 0.66 per cent., with the specific gravity  $d_{180} = 0.8732$ .

The pinenes obtained by fractional distillation from both oils, d-pinene from *E. dextropinea* (boiling point  $156^{\circ}$ , specific gravity  $d_{180} = 0.8629$ , optical rotation  $(\alpha)_{D180} = +41.2^{\circ}$ ) and l-pinene from *E. laevopinea* (boiling point  $157^{\circ}$ , specific gravity  $d_{190} = 0.8626$ , optical rotation  $(\alpha)_{D190} = -48.63^{\circ}$ ) are in accord with the hydrocarbons of the oils of pines and yield the derivatives characteristic for pinene. Although they are identical with pinene and differ from the pinene of turpentine oil only by a slightly higher rotatory power, Mr. Smith has preferred, on this account, to call the dextrogyrate pinene "Eucalyptene" and the laevogyrate "Eudesmene".

This multiplication of names for identical bodies cannot but meet with disapproval, for it restores the former confusion about these hydrocarbons. Provided that a hydrocarbon can be distinctly

<sup>1)</sup> Proc. Linn. Soc. N. S. Wales 26 (1898), 414.

<sup>2)</sup> Proc. Royal Soc. N. S. Wales 32 (1898), 195.

characterized by derivatives, a slight discrepancy in its optical rotation does by no means justify a distinction by a special name. There is particularly no reason for specifying d-pinene of *E. dextropinea*, since a higher rotatory power has been observed for the d-pinene of the oil of *Pinus Cembra*,  $[(\alpha)_D = +45.04^\circ]$ . For the pinene obtained from French turpentine oil, figures of optical rotation  $[(\alpha)_D = -43.4^\circ]$  have been found which closely approach those of the so-called "Eudesmene".

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On page 27 of our Report of October 1898, we referred to a paper of Mr. Parry on a new eucalyptus oil, said to be obtained from *Eucalyptus toxophleba*. We owe to Mr. E. M. Holmes, Curator of the Museum of the Pharmaceutical Society of Great Britain the information that Mr. Parry's nomenclature is not quite correct; it should be read *loxophleba* in place of *toxophleba*.

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There are but few plant genera whose essential oils present such a striking variety in their composition as that of eucalyptus. The new oils just mentioned, furnish an additional evidence of this fact. Cineol, citral, citronellal, cuminaldehyde and the hydrocarbons cymol, pinene, phellandrene and some other compounds have been recognized as constituents of the various eucalyptus oils. Further researches on the oils of this interesting genus may bring about the discovery of new constituents and we possibly may succeed in ascertaining, whether there exists an organic relationship in the composition of the various oils corresponding to their botanical relations, so that a more adequate classification of the species may become possible.

Attention was at first drawn to the oils containing cineol, and they soon found extended application for medication exclusively of other eucalyptus oils. As cineol is the only efficient constituent, the quality of these oils is estimated according to the percentage of cineol. It has recently been shown that the eucalyptus oils richest in cineol mostly are deficient in pinene and void of phellandrene, while the oils containing phellandrene are proportionately deficient in cineol and of inferior value. For medicinal purposes only those oils can come into consideration that are rich in cineol and void of phellandrene. The qualitative proof of the presence of cineol can be distinctly effected by means of the jodol- and bromide of hydrogen test, while unfortunately no reliable method has as yet been advanced for a quantitative estimate; the phosphoric acid method gives incorrect results<sup>1)</sup>. Phellandrene can be readily estimated by the well known reaction with sodium nitrite and acetic acid. All oils rendering this reaction are unfit for medicinal application.

<sup>1)</sup> Our Report, October 1898, p. 27.

All these eventualities could be obviated by introducing the pure cineol or eucalyptol in place of the oils with an ever changing amount of cineol.

**Geranium Oil.** The cultivation of geranium has been considerably extended in Algiers and as an additional explanation of the steady decline of values it is claimed that a greater yield of oil is obtained in consequence of better methods of raising the plants and distilling the material. As far as we have been informed about the geranium production and the appointments for distillation, they by no means excell by perfection. The price of the oil is a low one in consequence of overproduction.

Réunion oil, formerly much in favor, has become less in demand because it renders unsatisfactory results with transparent soaps. In view of the slight difference in price, African oil is preferred. The geranium cultivation on Réunion, moreover, has experienced a considerable reduction, since the plantation of vanilla has proved more remunerative and surer of profitable disposal.

Our supplies of East Indian oil of geranium (Palmarosa oil) have arrived and are of excellent quality. Upon several estimates they contain 92 per cent. of geraniol. The price of the oil is normal and no reduction is to be expected. We also have a fresh supply of the exceedingly fine Spanish oil.

**Guajacum-wood Oil.** In consequence of an accumulation of stock at various places the price of this oil is somewhat on the decline, the demand for and the interest in this commodity is decreasing. This is somewhat surprising, as the odor of the oil is exquisitely fine.

**Heracleum Oil.** When recently distilling the fruits of *Heracleum sphondylium*, we prepared, from the octylic alcohol first obtained by Zincke, octylaldehyde by oxidation with potassium chromate and sulfuric acid. This as yet unknown aldehyde has a strong odor recalling cœnanthol. Purified by its bisulfite compound, it boils at 60° to 63° unter 10 Mm. pressure; its sp. gr. is 0.827 at 15°. Octyl- $\beta$ -naphthocinchonic acid, obtained by the action of  $\beta$ -naphthylamine and pyrouvic acid according to Doebner's reaction, forms fine white crystals which when recrystallized from alcohol melt at 234°. Octylaldehyde combines with phosphonium iodide, forming a compound which melts at 115.5°.

**Hop Oil.** After having disposed of our stock of oil, we had to resort to the distillation of fresh hops of the harvest of 1898, the very best quality being worth *M.* 330.— per 100 kilos. This explains the considerable rise of prices. Corresponding to the quality of the raw material, our new distillate is of unexcelled quality.

**Hyacinth Oil "Schimmel & Co." synthetic.** Our readers will remember that we offered synthetic floral oils of our own make at

first in 1895 and 1896. Their preparation depended upon the systematic determination of the constituents of the odoriferous principles in the fresh flowers and the synthetic preparation of these constituents. In this way we succeeded in fully approaching to a perfect reproduction of the oils of jasmin, neroli and ylang-ylang, all received with unqualified appreciation and approval.

We now have the pleasure to record a further success upon this field by adding to the preceding synthetic oils of our make synthetic oil of hyacinth, fully equivalent in its exquisitely fine and natural perfume. It represents the natural odor of the flower to perfection and in concentrated form. The projected venture of manufacturing extract of hyacinth from the flowers in Holland would now turn out a failure. By dissolving a few drops of our "Hyacinth" in alcohol and comparing the odor of this solution on blotting paper with that of blooming hyacinths, the identity as to the fragrance between the two will be striking.

Our hyacinth is sold undiluted and its odoriferous intensity is very far reaching. 4 to 5 Gm. dissolved in 1 kilo of alcohol render an excellent triple-extrait; it is readily soluble in all liquids commonly used in perfumery, including fats and fatty oils. It has the characteristics of an essential oil, and a light-yellow color.

We have added this new product to our price-list and furnish gratis-specimens upon application.

**Jaborandi Oil.** There had been no interest in or demand for this oil for years when unexpectedly inquiries arose last November, after the experimental application of the oil in hypodermic injections. We then had no oil in stock but have since distilled new oil ready for orders.

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In our Report of April 1888, p. 44, we stated that the fraction of jaborandi oil with the boiling point above  $260^{\circ}$  contains a substance melting at  $27^{\circ}$  to  $28^{\circ}$ . In an oil distilled recently the amount of this body was so considerable that the oil solidified upon cooling. The solid part, after the removal of the fluid by suction, drying upon clay plates, and recrystallization from its solution in 90 per cent. alcohol, had the melting point of  $28^{\circ}$  to  $29^{\circ}$ , which is in accord with our former observations. This substance is evidently a hydrocarbon, not of the paraffine, but of the olefinic class of hydrocarbons, since its solution in petroleum ether absorbs with discoloration considerable quantities of bromine.

**Jasmin Oil.** Mr. Verley<sup>1)</sup> has isolated the odoriferous principle of the jasmin flowers by exhausting jasmin pomade by means of vaseline oil and treating this solution with acetone. After the evaporation of the acetone, a reddish oil remained having the intense

<sup>1)</sup> Compt. rend. 128, 314. — Bull. soc. chim. III, 21, 226.

odor of jasmin. The main part of the oil boils at  $100^{\circ}$  to  $101^{\circ}$  under 12 Mm. pressure and has the formula  $C_9H_{10}O_2$ . When oxidized, benzaldehyde or benzoic acid and formaldehyde respectively, when boiled with oxalic acid solution, styrolene alcohol  $C_6H_5.C_2H_3(OH)_2$  are formed. This admits the inference that the compound is the methylene-acetale of phenylglycol,  $C_6H_5.C_2H_3-\overset{O}{\underset{\text{O}}{\text{O}}} > CH_2$ . Mr. Verley calls the compound "Jasmal" believing it to be the odoriferous principle of jasmin flowers. "Jasmal" was obtained synthetically by heating phenylglycol with formaldehyde and sulfuric acid. It boils at  $101^{\circ}$  under 12 Mm. pressure and at  $218^{\circ}$  at common atmospheric pressure; its sp. gr. is 1.1344 at  $0^{\circ}$ .

Mr. Verley has also prepared in an analogous way the homologons of "Jasmal", aethylidene-, isobutylidene- and amylidene-acetales of phenylglycol; they are said also to have the odor of jasmin.

Messrs. A. Hesse and F. Müller<sup>1)</sup> have also prepared the oil of jasmin flowers in a somewhat similar way as Mr. Verley; they have rectified the oil, redistilling it with steam. They obtained 4 to 5 Gm. of oil from 1 kilo of jasmin pomade which they found to contain a high percentage of ester and to consist mainly of benzyl acetate and linalyl acetate.

Mr. Verley's "Jasmal" could not be found in the oil prepared by Messrs. Hesse and Müller. The phenylglycolmethylen acetale being not acted upon by alcoholic potassium, ought to have been discovered after the saponification of the oil, but there could not be found any trace of it. Upon boiling the oil with an aqueous solution of oxalic acid, no styrolenic alcohol was formed. Messrs. Hesse and Müller conclude therefrom that jasmin oil contains no phenylglycolmethylen acetale at all.

An investigation of jasmin oil was made in our research laboratories in 1895<sup>2)</sup>, affording us a fair insight into its constituents, whereupon we were able to manufacture our synthetic "Jasmin Schimmel & Co." Without entering upon the results of our examination, we may add the statement that we did not find in the oil isolated from jasmin pomade at that time any substance having the properties of "Jasmal", while we then also ascertained the presence of linalyl acetate and benzyl acetate as constituents of jasmin oil.

At the Saxon-Thuringian Exhibition at Leipzig in 1897, our exhibit also included benzyl acetate and benzylic alcohol<sup>3)</sup>, the latter

<sup>1)</sup> Berichte d. deutsch. chem. Ges. 32, 562.

<sup>2)</sup> In order to secure our right of priority, a report on these researches has been deposited with the legal authorities.

<sup>3)</sup> Boiling point  $88^{\circ}$  under 9 Mm. pressure. Melt. point of the phenylurethane  $77^{\circ}$  to  $79^{\circ}$ ; the latter compound is well suited for ascertaining the presence of benzylic alcohol.

being also a constituent of the oil. Both compounds have been added to our recent price-lists, because we believe them to be of useful application in perfumery.

**Juniper-berry Oil, our own distillate.** Since years we have not distilled so large quantities of this oil. The berries were of exceptionally fine quality, unusually rich in oil and juice. The article can be bought now to much advantage, while the juice has all been disposed of.

**Laurel leaves Oil.** At the distillation of laurel leaves a small quantity of oil was obtained which had a higher specific gravity than water and showed the presence of a phenol when agitated with a solution of caustic soda. The phenol separated by dilute acid corresponded in its qualities with eugenol, yielding also a benzoylcompound melting at 70°.

**Lavender Oil.** The values of this important commodity have been fully maintained since our last Report. The yield of the last harvest has passed into steady channels. Further quotations will depend upon the demand between now and the new crop.

At our purchases during the present season, we had occasion to further advance our knowledge in regard to the places where the oils containing a maximum amount of linalyl acetate are produced. In the present season several groups of distillers in various Departments have again applied to us to enter into direct dealings with them, such as we have been engaged in with others for years. In consequence, we are entirely independent of the firms of Southern France, and, as our quotations bear evidence, just as able as they to stand any competition.

**Lemongrass Oil.** In this article normal values have finally returned. Quotations in China vary between 2<sup>1</sup>/<sub>2</sub> and 2<sup>3</sup>/<sub>4</sub> d. per ounce, and transactions are said to be very dull, because large stocks are still laid up in London, checking any speculative tendency.

**Lepidium Oil.** This oil consists, according to the late Prof. A. W. von Hofmann's researches, of the nitrile of phenylacetic acid. Mr. J. Gadamer<sup>1)</sup> has recently ascertained that this is not quite correct and that the oil distilled from the fresh herb, carefully cut to pieces consists of benzyl-mustard oil. This oil is not ready-formed in lepidium, but results from the action of a ferment upon a glycoside. Since both are present in different cells of the plant, the formation of benzyl-mustard oil cannot take place before the cellular tissue is torn, so that the ferment and the glycoside come into contact and action upon one another. When the disruption of the cellular tissue is not brought about before the distillation, the ferment becomes inactive by the heat before this can break up the cells. The remaining

<sup>1)</sup> Archiv d. Pharm. Vol. 237. (1899), p. III.

glycoside then furnishes benzyl cyanide by decomposition. Prof. Hofmann, who obtained benzyl cyanide only, and no benzyl-mustard oil, has probably experimented with the plant without cutting it before distillation.

**Linaloe Oil.** The prices of this important oil have remained rather stationary and no further decline is to be expected in consequence of the increasing use and demand of this commodity. About 1200 kilos of oil said to be of excellent quality are on the way to us from Veracruz.

We used to distill this oil in considerable quantities in our establishments but have stopped doing so in consequence of a want of wood. The costs of transportation of the wood from the interior provinces of Mexico to the only accessible port, Veracruz, invalidates all further efforts for exportation of the wood.

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In our Report of April 1898, p. 32, we referred to a paper by Prof. J. Möller in Graz on *Lignum Aloës* and linaloe wood. The author has continued his studies about this subject and published them in a second report<sup>1)</sup>; they mainly take into consideration commercial aloe wood and are deserving of due interest, as also the illustrations of the anatomical structure.

**Mirban Oil (Nitrobenzol).** The value of this preparation has still more declined and its present low price is an unprecedented one. For this reason special discrimination is requisite when purchasing the article. We met in several cases with greatly inferior lots of the oil, although they were labelled as being well adapted for flavoring soaps.

We gratuitously report on specimens (at least 50 Gms.) sent to us for examination.

**Mustard Oil.** Prices continue to be rather stiff because favorable offers from Indian seeds have been wanting for some time so that Russian seeds which are higher in price had to be used for distillation. On several occasions we had to decline orders for large lots of oil.

**Neroli Oil.** Since petitgrain oil frequently is used for the sophistication of neroli oil, Messrs. Charabot and Pillet<sup>2)</sup> have submitted both oils to a comparative examination, mainly taking into consideration the principal physical properties and the amount of ester. They examined only such oils as were distilled by themselves at Cannes and found that the specific gravity of neroli oil ranges between 0.872 and 0.876, and that of petitgrain oil between 0.891 and 0.894. More considerable is the difference between the optical properties, particularly the rotatory power. Neroli oil is dextrogyrate (mostly  $+3^\circ$  and  $+4^\circ$ ), while petitgrain oil is lævogyrate. The rotatory

<sup>1)</sup> Pharm. Post 1898.

<sup>2)</sup> Bull. soc. chim. III. 19 (1898), 853.

power, therefore, renders a criterion for estimating the purity of neroli oil, because the addition of lemon, orange, or bergamot oils would raise the optical rotation, and that of petitgrain or linaloe oils would decrease it.

As the oils mostly used for adulteration have a high saponification figure, the percentage of ester may also serve as an indicator of the purity of the oil; this ranges, with neroli oil, between 10 and 20 per cent., with petitgrain oil between 50 and 70 per cent. An addition of oil of bergamot, consequently, raises not only the rotatory power, but also the percentage of ester.

The esters seem to be the main factors of the odoriferous qualities of neroli oil. Upon saponification both, neroli and petitgrain oil, lose their characteristic odor while that of linalool becomes strongly noticeable. The difference in the delicacy of the odor may be due to the presence of esters of the same alcohols in both oils, the acid constituents only being different. From saponified petitgrain oil geraniol could be isolated by means of the phthalic acid method. Linalool, also present to a considerable amount, did not react and could be detected in those parts of the oil unaffected by phthalic acid.

In an additional paper<sup>1)</sup> the authors report on the constituents of petitgrain oil. They specially endeavoured to ascertain the differences existing in the composition of the slightly dextrogyrate oil from Paraguay, and the lævogyrate oil distilled by themselves. They found that an oil distilled exclusively from the leaves and buds of the plant always is lævogyrate and still more so after saponification, since the acetic ester of 1-linalool has less rotatory power than the alcohol alone. The saponified oil yielded a lævogyrate fraction boiling below 185° containing but very little limonene, while a fraction obtained from saponified American oil was found to contain the dextrogyrate modification of limonene characterized by the tetrabromide. The difference in the optical rotation of the French and the American oil, is due to the amount of limonene; this likely originates from fruits incidentally admixed to the raw material.

As alcoholic constituents of the oil, 70 to 75 per cent. of linalool and 10 to 15 per cent. of geraniol were found to be present mainly as acetic esters. The remainder not passing over above 232° upon cooling, separated a solid mass, crystallizing from its solution in petroleum ether; the amount, however, was not sufficient for a closer examination. The not solidifying portion of the remainder rendered Wallach's sesquiterpene reaction.

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In consequence of an application for a patent by another firm we feel constrained to record for the protection of our rights of priority a discovery made by us in 1894.

<sup>1)</sup> Bull. soc. chim. III. 21 (1899), 73.

In the course of our researches on natural neroli oil in 1894, we observed a nitrogenous constituent of which the oil could be deprived by means of acids. We isolated the substance and found that it is an essential factor in the formation of the neroli aroma. Upon further researches, this substance proved to be the methylester of anthranilic acid. When pure, it distills at  $124^{\circ}$  to  $125^{\circ}$  under 9 Mm. pressure, solidifies after some time and melts at  $25.5^{\circ}$ . The solutions show a fine blue fluorescence. Upon analysis it proved to have the following composition:—

1.	0.1700	{	= 0.3985 Gm. $\text{CO}_2$ = 63.90 per cent. C
		{	= 0.0944 Gm. $\text{H}_2\text{O}$ = 6.17 " " H.
2.	0.1699	{	= 0.3956 Gm. $\text{CO}_2$ = 63.51 per cent. C
		{	= 0.0940 Gm. $\text{H}_2\text{O}$ = 6.15 " " H.
	0.2626 Gm.		= 0.025564 Gm. N = 9.73 per cent. N.

	found	calculated for $\text{C}_8\text{H}_9\text{NO}_2$
C	63.90	63.51 per cent.
H	6.17	6.15 " "
N	—	9.73 " "
		63.58 per cent.
		5.96 " "
		9.28 " "

The compound formed salts and double salts. The platinum salt gave the following figures:—

0.1727 Gm. rendered 0.0473 Gm. Pt = 27.38 per cent.
calculated for $\text{M} = 714 = 27.60$ " "

An estimation of the methyloxiide showed the platinum double salt to contain 7.72 per cent. of  $\text{OCH}_3$ :—

0.1920 yielded 0.1124 Gm. AgJ, corresponding to 7.72 per cent. of  $\text{OCH}_3$ .

Upon saponification of the substance by means of alcoholic potash, anthranilic acid melting at  $144^{\circ}$  to  $145^{\circ}$  was obtained.

The methylester prepared from anthranilic acid corresponded in all its properties to the substance isolated from neroli oil: boiling point  $132^{\circ}$  under 14 Mm. pressure, melting point  $25^{\circ}$ , sp. gr. 1.168 at  $15^{\circ}$ .

The solutions of the substance show a blue fluorescence, the odor is disagreeable, unless largely diluted, when the fine neroli odor appears.

For obvious reasons, indicated on page 74 of our Report of October 1897, we have preferred to abstain from a publication of our discovery, but had at the time deposited a full record of the same with our attorney.

The publication of our discovery does not, however, fully disclose the composition of our synthetic neroli oil, as the method of its preparation has since been improved in several important ways. A comprehensive paper on this matter will be published in the forthcoming issue of the "Journal für praktische Chemie".

**Orris-root Oil.** This important commodity is to be had at reasonable rates at present. All efforts of the producers in the neigh-

borhood of Florence to obtain higher prices have failed; the stocks in root are ample, so that the demand has greatly been checked and the last crop has met with few sales at low prices. The market has also been unfavorably retarded by distrustful reports.

The perfumery industry has had the benefit of these conditions of the market, since a liberal and comparatively cheap supply of orris oil is a great advantage to improve the quality of many products. In consequence we have received large orders for this oil from speculative dealers and manufacturers and are ready for orders for future delivery at the present low rates. As an evidence of the present cheap price we mention the following report of rates:—

The price of orris-root oil was:—

April 1 <sup>st</sup> 1893	. . .	Rs. 1600.—	per kilo
„ 1 <sup>st</sup> 1894	. . .	„ 1300.—	„ „
„ 1 <sup>st</sup> 1895	. . .	„ 1050.—	„ „
„ 1 <sup>st</sup> 1896	. . .	„ 1000.—	„ „
„ 1 <sup>st</sup> 1897	. . .	„ 900.—	„ „
„ 1 <sup>st</sup> 1898	. . .	„ 600.—	„ „
„ 1 <sup>st</sup> 1899	. . .	„ 500.—	„ „

In due justice to the interests of our customers we feel obliged to call their attention to this unusual chance.

**Parsley Oil from the fresh herb.** We have only 10 to 12 kilos of this much appreciated oil remaining. To secure part of this small stock, orders should reach us promptly. In using the oil in place of the fresh herb it should be remembered that 100 Gms. of oil represent 150 kilos of fresh herb.

**Patchouli Oil.** The cultivation of patchouli in Penang and the Straits Settlements has been so much extended that an excessive production seems to have taken place. The same may be said of patchouli oil and the utmost price-cutting prevails. This becomes patent from a review of the prices during the last 26 years:—

#### Prices of Patchouli Oil per kilo

January 1874	. . .	Rs. 75.—	January 1887	. . .	Rs. 105.—
„ 1875	. . .	„ 54.—	„ 1888	. . .	„ 100.—
„ 1876	. . .	„ 50.—	„ 1889	. . .	„ 70.—
„ 1877	. . .	„ 60.—	„ 1890	. . .	„ 60.—
„ 1878	. . .	„ 64.—	„ 1891	. . .	„ 56.—
„ 1879	. . .	„ 70.—	„ 1892	. . .	„ 50.—
„ 1880	. . .	„ 84.—	„ 1893	. . .	„ 40.—
„ 1881	. . .	„ 64.—	„ 1894	. . .	„ 32.—
„ 1882	. . .	„ 60.—	„ 1895	. . .	„ 30.—
„ 1883	. . .	„ 60.—	„ 1896	. . .	„ 40.—
„ 1884	. . .	„ 50.—	„ 1897	. . .	„ 54.—
„ 1885	. . .	„ 50.—	„ 1898	. . .	„ 48.—
„ 1886	. . .	„ 95.—	„ 1899	. . .	„ 34.—

Under these circumstances we cannot but recommend to lay in ample stock. Large shipments of choice leaves are on their way for us on the steamer "Flensburg".

**Peppermint Oil, American.** The excessive production has brought about an almost untenable condition which in time must make the cultivation and production of peppermint unprofitable. The price paid for raw oils in America amounts now to 70 cents to \$ 1.— per lb. Ten years ago no one would have thought such prices ever possible. They have been brought about mainly by Japanese competition, which has closed many channels to American oil. But American producers will also have to check excessive overproduction, for, although the consumption of oil of peppermint slightly increases from year to year, the present production is altogether disproportionate to the consumption.

**Peppermint Oil, German.** This oil was formerly distilled from leaves broken when drying the peppermint herb in Thuringia. It brought *M.* 30.— to *M.* 36.— per kilo. The demand increased, but at the same time American oil appeared in the market and checked German production by the ample supply of an equivalent oil. About 10 years ago the production in Thuringia had nearly stopped, but on account of its special properties the demand for German oil still prevailed. We have succeeded in obtaining an equivalent substitute by using American oil, which in its fine flavor so much approaches the German. The two grades offered by us as German oils are distillates made here from American raw oils. The cheaper quality is made from Western, the better one corresponding to the requirements of the pharmacopœia, from the finest Wayne County oil. Both are pure distillates from *Mentha piperita*. Although correct in regard to their origin, the denomination of these oils as "German peppermint oil" can not be justified any more. We have contemplated since some years to redress this anomaly. A recent paper by Mr. Conrady in the "Apotheker-Zeitung" No. 100 of 1898 furnishes us a welcome opportunity to drop for these two oils the name "German Peppermint Oil", hoping that others will follow suit.

Making special exception of our firm, Mr. Conrady expresses the opinion that much oil under the name of *Oleum menth. pip.* Ph. G. in the market consists of a mixture of American and Japanese oils. However near this may come to the truth, the fact is that such a mixture would not be passed by the authorities, because Japanese oil is not a distillate of *Mentha piperita* but of *Mentha arvensis* and has quite a different flavor. That such mixtures are sold and bought as peppermint oil is due to the prevailing tendency towards cheap grades particularly noticeable in the peppermint market.

The proposition of Mr. Conrady to sustain the peppermint cultivation in Germany by raising the requirements for the quality of officinal oil and thereby also to induce the payment of better

prices for the same is a point well taken but hardly possible to be realized. We have for years cultivated *Mentha piperita* on our plantations near Leipzig and know by experience that it is impossible even in seasons with normal and fair weather, to produce pure oil at less than *M.* 70.—. This article listed in our price quotations as Saxon peppermint oil, is, however, of unexcelled quality.

It may be added that our experiments with the culture of peppermint as yet are by no means concluded; new ideas for improvement have constantly been advanced, and particularly during the last season. Nevertheless, a competition with American peppermint cultivation is for several reasons impossible in Germany. Such a competition can only be made successful by obtaining oils of superior quality and at correspondingly higher prices. We have succeeded in realizing this ideal by means of modern manufacturing appointments not surpassed in any country. A drawback in all such generous efforts, however, consists in the indifference of the purchasers, who mostly place cheapness above quality.

The quantity of oil produced on our own plantations during the last season was approximately 350 kilos.

**Pine-needle Oil.** The quantity of oil distilled in Switzerland from the cones of *Abies pectinata* has been so considerable that there is no danger of a return of any scarcity in this commodity, as occurred last year. The demand for and use of this fine and very aromatic distillate has become immense. On account of its purity and agreeable odor it is much used in the preparation of the fine pine-needle syrups, "Tannenduft", and is also by far the cheapest. It is known in commerce by the not quite correct designation of "Pine-needle oil, extra fine", although we never fail to state in our price lists the real origin of the oil so as to avert any misconception.

The Siberian Pine-needle oil is more and more coming into demand and use, being the cheapest of this class of aromatic pine-needle oils that can be made and at the same time a perfectly pure distillate. All cheaper commercial oils of this class are more or less adulterated with oil of turpentine.

The Pine-needle oils from *Abies pectinata* (Edeltannen-Nadel-Oel) and from *Pinus pumilio* (Latschenkiefer-Oel) are always kept by us in stock and of the very best quality. The distillation of the latter kind in the Carpathian Mountains, planned some time ago, seems as yet not to have been started.

**Rose Oil, Bulgarian.** Matters in Bulgaria, instead of improving, have continued to retrograde and the rose oil trade is in a debased condition. Notwithstanding a notoriously deficient crop, the prices of Bulgarian rose oil have been still more reduced and so-called "guaranteed pure rose oil" is offered in Germany at *M.* 530.— per kilo. It is easy to calculate the resulting profit after having deducted expenses of production, commission &c.

The "Deutsches Handels-Archiv" contained in a recent issue the following note on the production of Bulgarian rose oil and on the price:

"The weather experienced in Bulgaria during last winter was unfavorable to the rose plantations. Frost and much cold weather without sufficient fall of snow prevailed, with occasional sudden changes to mild weather. A large number of the older plants were despoiled and the younger ones suffered considerable impairment. During the time of flowerage and distillation the weather was favorable, but the total yield fell short by at least one quarter of that of the preceding season and equalled, with about 400,000 meticals (about 2000 kilos), approximately one half of the total yield of the year 1896.

Some larger consignments for new oil have been contracted, but in consideration of the extensive old stock the prices of about *ℳ* 800.— per kilo fell short of those of the preceding year."

Notwithstanding such contradictory reports, there seems to be no chance to check the degeneration of the Bulgarian rose oil trade and the few upright firms are standing powerless in their efforts to ameliorate corrupt practices in the production of Bulgarian rose oil.

As much as chemistry has advanced in the practical application of methods for ascertaining the purity and quality of essential oils, they all are as yet insufficient for the examination of oil of roses, which, like its principal adulterant, consists approximately of 90 per cent. of geraniol. As is well known, the point of solidification can readily be maintained by artificial means, the odor fails to render any reliable criterion, and no other tests are as yet at our service. Adulteration therefore still has better chances with oil of roses than with any other essential oil and unfortunately the utmost use is made of this opportunity.

Our correspondents in Kazanlik, by many years' experience found to be thoroughly trustworthy firms, feel much provoked by the unfair and disreputable practices prevailing in the Bulgarian rose oil production and are anxious to abolish the corruption. The government also aims at the same end, fully aware of the inevitable final ruin of this fine and profitable industry. But in view of the prevailing lack of honesty and principles, at least in this industry, there seems to be little or no chance for a real and permanent improvement and a return to general fair dealing. The fact is that pure rose oil is quite scarce in Bulgaria and commands far higher rates than those mentioned above. Formerly the sophistication was practised mainly by the exporters and jobbers, it has now extended to the distillers too, who are adding palmarosa oil to the flowers in the stills.

The March number of the "Deutsches Handels-Archiv" contains the following additional note about the Bulgarian rose oil production:

"The price of pure Bulgarian rose oil, which was quoted in August 1898 at *ℳ* 800.— per kilo, has declined during last fall to *ℳ* 690.— in consequence of less demand and a considerable stock remaining from last year. Quotations in foreign markets show even still lower rates, but they cannot apply to real pure rose oil.

The cultivation of roses started at various places in Anatolia (Asia Minor) is making gratifying progress. The yield of the crop of the present year

amounted to 700 metikals (each  $3\frac{1}{2}$  kilos); but this trial experiment cannot be taken as furnishing a standard inasmuch as the extensive plantations at five various places in Anatolia have not yet been ready for distillation. For, most of the two year old bushes from which a considerable crop of flowers might have been obtained this year, have been used for extending the plantations, and the remaining crop of flowers was mainly used for the distillation of rose water in order to partly defray the expenses. The farmers engaged in this cultivation have only small areas of land at their disposal. But when all this will be under cultivation, the Anatolian production of rose oil may before long rise to considerable importance, if at first not on account of the quantity, at least because of the quality of the oil. We have as yet had no opportunity to obtain specimens of Anatolian rose oil, but experts claim that its odor is of superior fineness. The well known integrity of the Anatolian farmers, who have emigrated from Eastern Roumelia, may be a guarantee against dishonest practices so ruinously prevailing in Bulgaria.

The Turkish government favors the cultivation of roses and the introduction of this industry and has granted to the farmers exemption from taxes and internal revenue for some years (yet 5 years). The farmers feel encouraged by this privilege and trust the more in the ultimate success of their efforts since a prominent German export firm, familiar with the cultivation of roses and their distillation, has engaged in assisting them by their guidance in systematic methods and practices in the culture of roses."

**Rose-wood Oil.** We have distilled a specimen of wood received from Teneriffe and said to be obtained from *Convolvulus scoparius*. The odor of the oil by no means came up to our expectations and the high price asked for the wood is entirely out of proportion to the aroma of the wood. Its optical rotation is  $+1^{\circ}30'$ , its sp. gr. 0.951 at  $15^{\circ}$ , the figure of saponification = 0. The oil dissolves in 10 volume-parts of 95 per cent. alcohol. After acetylation the figure of saponification found was 151.3.

**Rosemary Oil.** Notwithstanding the low quotations, there is very little demand for Dalmatian oil. According to reports in newspapers the attention of the government is said to have been called to the prevailing neglect of the rosemary industry in Dalmatia. The plants cover large areas both of the mainland and the islands, but the inhabitants have not the means for procuring modern stills; with their traditional primitive appliances most oil is lost at the distillation.

**Sandal-wood Oil, East Indian.** At the recent auction at Mysore quite an assortment of choice woods was offered for sale. According to the new classification the following quantities of ten different sorts were offered:—

Hunsur	Nov. 21 <sup>st</sup>	. . .	Tons about	375
Seringapatam	" 24 <sup>th</sup>	. . .	" "	300
Bangalore	" 28 <sup>th</sup>	. . .	" "	150
Hassan	Dec. 2 <sup>nd</sup>	. . .	" "	225
Chickmagalur	" 15 <sup>th</sup>	. . .	" "	200
Shimoga	" 9 <sup>th</sup>	. . .	" "	375
Sagar	" 13 <sup>th</sup>	. . .	" "	225
Tirthally	" 19 <sup>th</sup>	. . .	" "	150

Total: Tons about 2000

All of these except 203 tons were sold, and this balance soon also found purchasers. They brought about the same prices that were paid last year and the price of sandal-wood oil is not likely to experience any change.

The total export of sandal-wood (Timor) from Dutch India consisted in

1897, of 325,997 kilos, worth Fl. 45,639.—,  
and from the port of Makassar

in 1897 . . . . . 84,536 kilos  
„ 1896 . . . . . 71,465 „

Little of this sort of wood is shipped to Europe, the greatest portion remains and finds use in Asia. As there hardly exists a difference in price between the oils of the East Indian and the Makassar woods there is little demand for the oil of the latter.

In our last Report we mentioned an Australian sandal-wood oil. It seems that larger lots of this oil have not arrived since, at least our efforts to obtain some original bottles of it in England have been unsuccessful.

East Indian Sandal-wood oil consists of 94 to 98 per cent. of alcoholic constituents, commonly called santalol. This is obtained by saponifying the oil and by subsequently rectifying it by distillation under low pressure or with overheated steam. We were the first to bring santalol prepared in this way into commerce and have exhibited this product at the Saxo-Thuringian Exposition at Leipzig in the summer of 1897. At a recent comparative examination of our own and a competitive product, the oils were found to fairly match each other in regard to the boiling point and specific gravity.

Marking	Specific gravity	Figure of saponification	Boiling point 11 mm pressure	Percentage of santalol calculated for $C_{15}H_{26}O$
1. Our product. . . . .	0.979	1.34	168°—169°	98.8
2. „ „ exhibited in 1897 . . . . .	0.980	6.3	—	100.3
3. Competition product	0.979	8.0	168°—170°	99.3
4. „ „	0.979	3.5	—	100.1

As is to be seen from these figures, the saponification in no case has been complete. In order to prepare pure santalol we proceeded in the following way: 100 Gm. of East Indian sandal-wood oil of the sp. gr. of 0.977 and the saponification figure of 4.4 and containing 94.1 per cent of santalol were heated to 80° with an equal weight each of phtalic acid anhydride and benzol upon a

water-bath for one hour; the acid esters formed were combined with alkali and dissolved in an excess of water. The aqueous solution was deprived of the non-alcoholic constituents by agitation with ether repeated three times and the acid esters were separated by the addition of dilute sulfuric acid; subsequently they were saponified by means of alcoholic solution of potassium hydrate, and the santalol set free was deprived of adhering alkali and alcohol by washing it with water. By fractionating under 13 Mm. pressure the following fractions were obtained:—

1. 170° to 172°; sp. gr. 0.978; opt. rot. — 15°22'
2. 172° „ 172°; „ „ 0.979; „ „ — 18°0'
3. 172° „ 172°; „ „ 0.979; „ „ — 26°47'

None of these fractions rendered a figure of saponification. The product obtained amounted to 85 per cent. of the oil used. The odor slightly resembles that of sandal-wood oil. Although this product may be devoid of esters and other “non-alcoholic” constituents, it can by no means be considered a definite chemical compound for the reason that its optical rotation reveals too considerable differences between the three fractions.

In order to settle this point, fraction 1 was furthermore submitted to fractional distillation and a substance obtained which boiled at 165° and 167° under 13 Mm. pressure and had the sp. gr. 0.97 and the opt. rot. — 7°20'. Treated in the same way, fraction 3 rendered a product having a considerably higher boiling point, namely 173° under 13 Mm. pressure, the sp. gr. 0.979 and the opt. rot. — 32°36'. A substance yielding upon fractionation two products so much differing cannot be considered an individual chemical compound. Santalol, therefore, is a mixture of two sesquiterpene alcohols of which the one with a lower boiling point seems to be optically inactive or possibly dextrogyrate, while the other having a higher boiling point is strongly laevogyrate. Further researches will lead to the determination of the chemical composition and the properties of these alcohols.

The portion of the oil, not acted upon by anhydric phthalic acid and remaining behind in the ether used for washing, was deprived of the ether by distillation, and of any phthalic acid anhydride still left by repeated agitation with hot water. It was subsequently submitted to fractional distillation under 11 Mm. pressure:—

- |                                                     |                |
|-----------------------------------------------------|----------------|
| 1. 132° to 164°; sp. gr. 0.955; $\alpha_D$ — 16°8'; | 9.0 Cc.        |
| 2. 164° „ 172°;                                     | 3.0 „          |
| 3. 172° „ 200°;                                     | 2.0 „          |
|                                                     | Residue: 1.0 „ |
|                                                     | 15.0 Cc.       |

Fraction 1 is the main fraction, having the saponification figure of 33.6, which calculated upon 9.0 Cc. shows it to contain 1.34 Gm. of santalyl acetate. As the 100 Gm. of oil originally used

contained 1.76 Gm. of santalyl acetate at a saponification figure of 4.4, little ester has been lost by treating the oil with phthalic acid anhydride; this may, however, be contained in fractions 2 and 3, which could not be submitted to a closer examination on account of their small quantity.

It is remarkable that the esters contained in East Indian sandal-wood oil have a lower boiling point ( $132^{\circ}$  to  $164^{\circ}$  under 11 Mm. pressure) than the sesquiterpene alcohols. To all appearances they contain other alcoholic constituents than the sandal alcohols.

In conclusion it may also be stated that santalylphthalic acid could not be made to crystallize, even after it had been kept at a low temperature for weeks. Santalylphthalate of silver melts at about  $50^{\circ}$  and is difficult to be recrystallized.

Hitherto West Australian sandal-wood oil was believed to be obtained from the wood of *Santalum cygnorum*. According to a statement of Mr. Parry<sup>1)</sup> the wood of at least three other species is used for distilling the oil, *Santalum lanceolatum*, *S. acuminatum* and *S. persicarum*. The woods are indiscriminately collected and used for distilling.

Mr. Parry examined four specimens of dark colored sandal oil which had been distilled from older woods of uncertain derivation. The oils were slightly dextrogyrate and somewhat heavier than usually ( $d_{15}^0 = 0.9632$  to  $0.9650$ ). The percentage of ester was between 1.15 and 1.66. After acetylation their odor was somewhat different from that of common Australian oil and the acetyl figure of an average specimen of the oils mixed answered to a percentage of 75.5 of alcohol (calculated for  $C_{15}H_{26}O$ ). Other reactions seem, however, to take place at the acetylation, so that the acetyl figure cannot be regarded as correctly indicating the amount of alcohol really contained in the oil.

The oil contains furthermore an as yet undefined aldehyde of a characteristic odor, which disappears on the action of reducing agents. Mr. Parry is of the opinion (but an erroneous one) that the so-called "pure santalol" of the German market is nothing else but a sandal-wood oil which has been submitted to a process of reduction. The specific gravity of the reduced oil is higher than that of the original; on the other hand the acetylated reduced oil has a lower specific gravity and requires less alkali for saponification than the acetylated unreduced oil.

There is as yet no way for exactly ascertaining the reactions taking place at the reduction and the subsequent acetylation, as our knowledge about the constituents of sandal-wood oil still is an imperfect one. The term of "santalol" especially is as yet an altogether

<sup>1)</sup> The Chemist and Druggist. 53 (1898, II), 708.

indefinite one and a closer examination of sandalwood oil is still remaining a desideratum.

**Sandal-wood Oil, West Indian.** The supply of this wood was a plentiful one, although the difficulties of transportation from the interior to the Venezuelan ports are said to increase.

The demand for the oil was a brisk one.

Mr. Holmes, Curator of the Museum of the Pharmac. Soc. of Great Britain, has published an interesting paper<sup>1)</sup> on the so-called "West Indian sandal-wood". The geographical distribution of the genus *Santalum* made it more than doubtful whether this wood may be derived from a *Santalum*. Mr. Holmes obtained by the aid of the British Consulate at Puerto Cabello leaves and branches of the tree, while we succeeded, after several years' efforts, in getting a branch with flowers, as also a number of fruits of the tree. Former examinations of Messrs. Kirkby and Petersen had established the fact that the plant is not a *Santalacea*, but very likely a *Rutacea*. Subsequently, when we had obtained the fruits, and a re-examination in the Botanical Garden at Cambridge had brought out the fact that the plant did not belong to any genus of *Rutaceae* described in English botanical literature, Mr. Holmes supposed it to be a new genus. Dr. Urban in Berlin however showed that the plant belongs to the genus *Amyris* and has identified it as *A. balsamifera*. This genus has thus far been classified by English botanists among the *Burseraceae*, in Germany, however, and correctly as admitted by Mr. Holmes, among the *Rutaceae*. The only differences between the Venezuelan plant and the specimens of *A. balsamifera* in the Kew Garden Museums consist in a more elliptical fruit and the relative length of the stamens, of which 4 are longer than the other 4. As there is no valid reason why there should not be a slight difference in the shape of the fruits, and as the difference in the relative length of the stamens may have been overlooked at former botanical examinations, Mr. Holmes also feels disposed for the present to consider *A. balsamifera* as the tree furnishing West Indian sandal-wood.

**Savin Oil.** Professor Wallach has shown this oil to contain cadinene, and, as stated in our Report, October 1895, p. 44, it also contains a considerable amount of an alcohol partly free, but to a larger extent present in the form of acetic ester. This alcohol, to which we accorded the formula  $C_{10}H_{18}O$ , has recently been examined by Professor Fromm in Freiburg i. B.<sup>2)</sup> The acetic ester can be isolated by careful fractionation of the oil. The alcohol readily obtained from the ester, is called "sabinol" by the author, it boils at  $208^{\circ}$  to  $209^{\circ}$ , has the formula  $C_{10}H_{16}O$  and is contained in savin

<sup>1)</sup> Pharmac. Journ. (London) 1899. No. 1491.

<sup>2)</sup> Berichte d. deutsch. chem. Ges. 31 (1898), 2025.

oil, mainly combined with acetic acid and to a lesser extent with an acid having a higher boiling point ( $247^{\circ}$ ). Its odor is somewhat like that of tanacetone; it is unsaturated and yields quantitatively a two-basic acid  $C_9H_{14}O_4$ , melting at  $140^{\circ}$  when oxidized by means of solution of potassium permanganate. This acid is identical with  $\alpha$ -tanacetogenedicarboxylic acid, obtained by Dr. Semmler from tanacet-ketocarboxylic acid. When heated with acetic anhydride, "sabinol" renders an acetate having the odor of oil of savin; at the same time the elimination of the elements of water and the formation of a hydrocarbon, boiling at about  $175^{\circ}$ , takes place; the latter is also formed by the action of chloride of zinc upon the alcohol.

Tanacetone (thujone) and "sabinol", therefore, seem to be related compounds corresponding to the close botanical relation of *Thuja occidentalis* L. and *Juniperus sabina* L.

**Snake-root Oil** see **Asarum Oil**.

**Spearmint Oil.** This oil is offered in unobjectionable quality at cut-rate prices. American competition also has successfully repressed all other products.

**Star-anise Oil.** By the vigorous measures taken upon our initiative by some of the most influential firms of Hongkong, the adulteration of oil of star-anise seems to have been largely checked in China; at least a sufficiently large stock of good oil solidifying at  $+15^{\circ}$  to  $17^{\circ}$  is now stored in Hongkong. We are in receipt of the following information from that commercial centre, dated November 25<sup>th</sup>, 1898:—

"It may be of interest to you and your customers to know that all oil of star-anise obtained during this season from the province of Lungchow has a solidifying point of  $15.5$  to  $17^{\circ}$  C. We have been called upon by a number of Chinese dealers to examine samples of their oils, and no oil derived from that province was found to be of inferior quality, while all oils obtained from the province of Nam-Ning on examination proved to be very unsatisfactory, solidifying at  $10^{\circ}$  to  $14^{\circ}$  C. Since the Chinese dealers cannot well dispose of such inferior oil at home and only at much reduced rates, they prefer purchasing their stock at Lungchow where they are surer to get a good oil. For the present this and the relatively low prices of star-anise oil are said to be the reasons why the distillation of the oil has altogether ceased in Nam-Ning, and the fruits are exported. If such are the facts, it is to be expected that inferior oils will disappear from the markets, except, perhaps, a few lots still left in the hands of distillers. Since the province of Lungchow can well supply the entire demand for this commodity, whenever the harvests have been fairly good, this change in the province of Nam-Ning will not exercise any notable influence upon the prices of the oil; they are likely rather to decline in consequence of the increasing supply of star-anise fruits."

If the distillation of star-anise in the province of Nam-Ning should be entirely discontinued, the credit of Chinese oil of star-anise may soon be restored. The rule, however, should in any case be maintained to purchase this oil only upon the basis of a definite point of solidification, by no means lower than  $15^{\circ}$  C.

We have received the following statistics in regard to the total shipments of star-anise oil from China and Tonkin during the last 5 years:—

	1893/94	1894/95	1895/96	1896/97	1897/98
Packhoi und Lappa (Hongkong and Macao) . . .	862	1998	489	2369	1398
Haiphong (Tonkin) . . . .	—	—	13	435	399
Total in piculs at 2 boxes:	862	1998	502	2804	1797

At present a sharp competition in prices takes place between China and Tonkin. It will, however, be different from what it has been heretofore, when no strict discrimination was made between pure and adulterated oil, while we now have a definite criterion for estimating the quality of the oils.

The present conditions of the star-anise oil market are normal and it is safe to invest in larger purchases.

Mr. J. C. Umney<sup>1)</sup>, induced by a recent paper of Mr. J. B. Simon<sup>2)</sup>, is of the opinion that the slight differences recently observed in star-anise oils, are caused by a different raw material, since oils are also distilled from the leaves and twigs of star-anise. This deviation from the traditional mode of obtaining the oil from the fruits exclusively, was first practised by the natives of the Po-Sé district, but seems to be quite common now. Mr. Umney has examined several of these oils distilled from leaves; they have almost the same odor as the oils from the fruits, their specific gravity is 0.9878 at 15.5°, the rotatory power +1°; but a considerable difference exists in the point of solidification, as this oil frequently remains fluid even at +8°. It was ascertained by fractionate distillation that these oils are richer in anise aldehyde, which usually is formed in the oils of anise and of star-anise after some time on account of the gradual oxidation of anethol; by this process a decrease of the point of solidification takes place. Mr. Umney deems it not unlikely that the presence of a slight amount of anise aldehyde contained in oil of star-anise may be the cause for the difference in the odor of the oils of anise and of star-anise. (Compare our Report of October 1898, p. 42.)

**Storax Oil.** On account of an improved method of preparation, this oil can now be supplied considerably cheaper.

**Thyme Oil.** Mr. Labbé has furnished a contribution to the knowledge of this oil<sup>3)</sup>. Hitherto pinene, cymol and borneol, and of the phenols, thymol and carvacrol, had been found to be contained in oil of thyme; very likely there is also present some linalool<sup>4)</sup>.

<sup>1)</sup> The Chemist and Druggist 54 (1899, I), 323.

<sup>2)</sup> Ibidem 53 (1898, II), 875.

<sup>3)</sup> Bull. soc. chim. III. 19 (1898), 1009.

<sup>4)</sup> Report of Schimmel & Co., October 1894, p. 57.

Mr. Labbé obtained 30 per cent. of phenols, which he considers to consist mainly of thymol. By agitating the oil with caustic potash, he deprived it of the phenols and divided the remainder into its component parts by fractionate distillation, using a Le Bel dephlegmator. Such he found to be: A hydrocarbon boiling at  $155^{\circ}$  to  $158^{\circ}$ , yielding a nitrosochloride melting at  $106.5^{\circ}$  showing that this hydrocarbon is no pinene (the different result obtained by Schimmel & Co. is in Mr. Labbé's opinion likely due to an adulteration of the oil examined, with oil of turpentine); furthermore, a hydrocarbon with the same boiling point as menthene which yields a nitrosochloride melting at  $113^{\circ}$  and cymol when oxidized by potassium permanganate solution; and finally a mixture of several cymols, distilling between  $174^{\circ}$  and  $184^{\circ}$ . The fraction obtained between  $195^{\circ}$  and  $200^{\circ}$  containing linalool was converted into geranyl acetate by the action of acetic anhydride. After the saponification the geraniol was identified by the geranylphthalate of silver melting at  $133^{\circ}$  C. The fraction obtained between  $200^{\circ}$  and  $215^{\circ}$  contains borneol, which could not be isolated, and therefore the alcohol was converted into and identified as, camphor by the action of chromic acid mixture. In the fractions boiling above  $215^{\circ}$  a small amount of carvacrol could be determined which had escaped the action of caustic potash.

According to Mr. Labbé the average composition of oil of thyme is:—

Thymol . . . . .	30 per cent.
Hydrocarbon, boiling point $155^{\circ}$ to $158^{\circ}$ ,	17 „ „
Menthene . . . . .	15 „ „
Cymol . . . . .	21 „ „
Linalool . . . . .	5 „
Borneol . . . . .	8 „ „

At the conclusion the author expresses the opinion that it is not quite correct to estimate oil of thyme solely by the amount of phenols contained therein, without taking into consideration also those constituents which exercise some influence upon the odor of the oil, viz. linalool and borneol.

We beg leave to add a few critical remarks to this paper. Regarding the presence of pinene in oil of thyme, Mr. Labbé would have succeeded in proving the presence of this hydrocarbon, if he had converted the nitrosochloride melting at  $106.5^{\circ}$  into nitroso-pinene by treating it with alcoholic potassa solution, or else into the characteristic nitrolamines by means of piperidine or benzylamine. As is well known, the nitrosochlorides are not adapted for identification on account of their readiness to decompose. From the determination of the melting point of the nitrosochloride alone the presence of a hydrocarbon different from pinene cannot be inferred.

It is not unlikely that oil of thyme contains menthene, especially as Mr. Charabot<sup>1)</sup> has found pulegone to be a constituent of the oil of *Thymus virginicus*. The melting point of the nitrosochloride, 113°, also points to menthene, but the further evidence adduced in favor of the presence of this hydrocarbon is not valid, because cymol has as yet never been obtained by the oxidation of menthene by means of permanganate. The fact in this case is that the respective fraction is a mixture of two hydrocarbons, of which the one with the lower boiling point is destroyed by the oxidizer, while cymol remains behind. This result, however, furnishes no evidence of the presence of menthene and the question whether this hydrocarbon is really contained in oil of thyme still remains an open one.

The most valuable constituents of thyme oil are without doubt the phenols thymol and carvacrol, and the quality of the oil will in the first place depend upon their percentage.

**Vetivert Oil.** Our stock of this oil was disposed of before new shipments arrived, so that we were unable for some time to fill orders. Meanwhile we have received after unusual delays at the East-Indian coasts shipments of new raw material and now can supply any demand. On this adverse occasion it became patent that customers used to our product cannot well get along with imported oil.

**Wax Oil.** The opinion seems to prevail that this oil, obtained by the dry distillation of wax, possesses the odor of bees' wax and can be used to impart this fragrance to vegetable waxes. We are constantly asked for samples, the result being disappointment and unavailing correspondence.

We therefore beg once more to state that wax oil, being the product of dry distillation, has a disagreeable, empyreumatic odor which has not the slightest relation or similarity to bees' wax or honey. The oil is, as far as we are informed, only used for making some ointments, but otherwise belongs to the obsolete remedies.

**Wintergreen Oil.** By the aid of our New York firm we are regularly and fully supplied with the natural oil put up in the well known 6 lbs. glass bottles. They are much to be preferred to the former tins since this oil is very apt to be impaired by a long contact with metals.

The price of the oil is a very cheap one.

The researches about the distribution of methyl salicylate in plants have been continued in the agricultural laboratory of the Botanical Garden at Buitenzorg in Java. By these investigations the ester has

<sup>1)</sup> Revue générale de chimie pure et appliquée I (1899), 59. — See also Pulegone in this Report.

lately been found in a large number of plants. Besides the natural orders mentioned in our Report of October 1898 page 45, representatives of the following families have been found to contain methylsalicylate: *Acanthaceae*, *Artocarpaceae*, *Apocynaceae*, *Asclepiadaceae*, *Bixaceae*, *Bignoniaceae*, *Burseraceae*, *Chrysobalanaceae*, *Dilleniaceae*, *Memispermaceae*, *Myristicaceae*, *Myrsineae*, *Pomaceae*, *Samydaceae*, *Sapotaceae*, *Styraceae*, *Violaceae*.

**Ylang-Ylang Oil.** By straining all their energies and resources our friends in Manila have succeeded in continuing the distillation under great difficulties so that so far all their regular customers have received a full supply of the "Sartorius" brand of oil. We recently received via Marseilles 14 boxes. Further shipments have not been announced.

It nevertheless remains a question whether it will be possible to continue distillation under the altered conditions. This depends entirely upon the further evolution of matters in Manila. Since this industry is mainly carried on by German firms, who in any emergency expect to receive due protection, it is to be hoped that the danger of a long interruption will be averted. Should such a one, however, occur, the synthetic product will creditably fill the place of the natural oil.

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## Novelties.

One of the objects of the researches constantly carried on in the laboratory of agricultural chemistry of the Botanical Garden at Buitenzorg, conducted under the directorship of Dr. van Romburgh, consists in finding new plant products and among them essential oils which may be useful in industry and the arts. To former results of this steady work, some recent ones have been added. Of these we notice the following report on the oil of *Alpinia malaccensis* Rosc. The rhizomes of this *Zingiberacea*, growing wild in the neighborhood of Buitenzorg and called "*Ladja goah*", yield on distillation about 0.25 per cent. of a colorless oil with an agreeable odor and the sp. gr. of 1.039 to 1.047 at 27°. It is slightly dextrogyrate (0.25° to 1.5° in a 200 Mm. tube) and solidifies almost entirely at a slight refrigeration. The solid substance is the methylic ester of cinnamic acid, in this case met with for the first time in an essential oil. The leaves of this plant also yielded an essential oil rich in methylcinnamate.

We owe to the kindness of Dr. van Romburgh a specimen of this oil, which forms a solid mass at moderate temperature and has the pleasant odor of methylcinnamate with a slight by-odor recalling that of borneol.

Cinnamic acid-esters are very likely also contained in the oil of another *Alpinia* species, *Alpinia nutans* Rosc., because the fraction of this oil, passing over at 255° to 265°, yields upon saponification an acid, melting at 134°, which doubtless is identical with cinnamic acid.

In addition to these notes we append from the interesting and valuable annual Report of the Buitenzorg Garden a statement of plants which upon distillation yield hydrocyanic acid. To the ones long since known the following plants have recently been added:—

<i>Passiflora laurifolia</i> L.	<i>Passiflorae</i>
„ <i>hybr. Imp. Eugénie</i>	„
„ <i>princeps</i> Lodet.	„
<i>Tasconia spec.</i>	„
<i>Plectronia dicocca</i> Brck.	<i>Rubiaceae</i>
<i>Prunus javanica</i> Mic.	<i>Amygdaleae.</i>

The two last named plants contain at the same time hydrocyanic acid and benzaldehyde. The latter alone, with some methylsalicylate and sometimes with traces of salicylaldehyde, was found to be contained in the leaves of *Homalium tomentosum* Benth. (*Samydaceae*), and also in two species of *Memecylon*.

### Notes on recent papers concerning terpenes and essential oils.

R. Mauch<sup>1)</sup> has instituted a series of experiments in regard to the physical and chemical properties of chloralhydrate including its deportment towards essential oils. He found that terpenes and those oils consisting mainly of terpenes are very little soluble in dilute aqueous solution of chloralhydrate, while a solution containing 80 per cent. of the same is an excellent solvent for oils containing oxygenated compounds. The solubility, however, decreases rapidly and proportionally to the concentration of the solution, but even a 60 percent. solution still dissolves a considerable amount of oil. Some of the oils, as for instance oil of gurjun-balsam, of peppermint and others, render remarkable color reactions with aqueous solutions of chloralhydrate as well as with those acidulated with hydrochloric acid.

Oils containing anethol, like those of anise and star-anise, render a jelly-like mass with an 80 percent. solution of chloralhydrate, while citral and citronellal after some time form crystalline compounds whose composition has not yet been investigated.

<sup>1)</sup> Inaugural-Dissertation. Strassburg 1898.

The property of oil of turpentine to acquire oxidizing powers by the absorption of oxygen has led to frequent inquiries to ascertain in what way oil of turpentine is acted upon in this process and again in what condition the oxygen acts. Experiments on auto-oxidation made some time ago by Messrs. Engler and Wild had shown "active" oxygen to be chemically fixed, but that it nevertheless is readily disengaged. Experiments by Messrs. Engler and Weissberg<sup>1)</sup> indicate that the processes are of the same nature with active turpentine oil. They ascertained that the oxygen of the active oil of turpentine is neither ozone nor atomic oxygen, and that the oxidizing effect of active oil of turpentine cannot be due to hydrogen peroxide because it is completely devoid of this compound. Although the compound formed at the absorption of oxygen by the oil is not yet known, it very likely consists of a peroxide.

It was also observed that the activity of the oil does not increase in the ratio of the oxygen absorbed, because part of the "active" oxygen is taken up by oxidizing the oil itself. In the same way as the supposed peroxide acts upon oil of turpentine, it oxidizes other substances. It furthermore has been shown that the temperature has an influence upon the process of activation; the greatest activation of the oil takes place at 100°, beyond that temperature it decreases and altogether stops at 160°. Existing activity is destroyed at this temperature as well as by heating the oil for some time to 80° to 100°. The oxygen set free is used up for the oxidation of the turpentine oil.

The investigators will continue their researches with the particular aim to ascertain the nature of the compound containing the active oxygen.

The desideratum to detect addition-products of the terpenes which upon disengagement of the added components yield the terpenes in a pure state, has as yet not been realized. Although addition-products of terpenes are known, the hydrocarbons prepared from them, however mostly are not identical with the original ones or else they contain by-products which cannot readily be removed.

So simple a separation as can be effected with some aromatic compounds by means of picric acid is not practicable with the terpenes. Pertaining experiments with pinene, limonene and others have proved unsuccessful. For the present we therefore have to resort to halogen-hydrogen addition-products and to regenerate therefrom the hydrocarbons by displacing the halogen-hydrogen, or else to employ hydroxylic compounds, namely alcohols, and to convert them into hydrocarbons by the elimination of water, sometimes even by the intermediate transformation to the chloride of the alcohol. Both methods have their shortcomings, but the latter one, admissible

1) Ueber die Activirung des Sauerstoffes. II. Der active Sauerstoff des Terpentins. Berichte d. deutsch. chem. Ges. 31 (1898), 3046.

only to a limited degree, renders purer products. The desideratum to obtain by a simple method all terpenes in a pure state, therefore, may remain unsolved for some time longer.

The addition-products obtained from formaldehyde and pinene, limonene and dipentene, recently described by Mr. Kriewitz<sup>1)</sup> also do not answer the above mentioned purpose. These compounds are formed when the terpenes are heated for some time at 170° to 190° in a closed tube with calculated quantities of paraformaldehyde in alcoholic solution. They are dense, nearly colorless liquids with high boiling points (pinene 232° to 236°; limonene 246° to 250°; dipentene 242° to 248°) and hygroscopic, although insoluble in water. They form crystallizing addition-products with halogen-hydrogen acids, thereby proving to be, like the terpenes, unsaturated compounds. They otherwise act like alcohols and can be converted into acetyl and benzoyl compounds by boiling with acetic anhydride or by the action of benzoic chloride and alkali. The addition-products obtained from the active terpenes pinene and limonene correspond in their optical rotation to the original product.

A paper by Prof. A. von Baeyer on the transformation of terpenes into benzol-derivatives was mentioned in our Report of October 1898, p. 47. By action of zinc dust and hydrochloric acid upon brominated sylvestrenedi-hydrobromide, this investigator has now succeeded<sup>2)</sup> in eliminating the bromine contained therein in the form of hydrogen bromide. The final product obtained is m-cymol, which yields oxyisopropylbenzoic acid melting at 123° to 124°, and isophthalic acid when oxidized by means of a chromic acid mixture.

Prof. Wallach some time ago observed that at the oxidation of fenchene under certain conditions two different acids  $C_{10}H_{16}O_3$  may be formed, of which the one melts at 137° to 138°, the other at 152° to 153°. As recently has been ascertained<sup>3)</sup>, this is due to the fact, that when fenchene is prepared from fenchylchloride, two hydrocarbons may be formed according to the prevailing circumstances, having opposite rotatory powers, and of which the one yields upon oxidation by means of permanganate solution the acid melting at 137°, the other the acid melting at 152°. Both acids are optically active, but have opposite rotatory powers of unequal intensity.

When D-l-fenchylalcohol<sup>4)</sup> is converted into fenchylchloride by the action of phosphoruspentachloride, the resulting chloride is always

<sup>1)</sup> Berichte d. deutsch. chem. Ges. 32 (1899), 57.

<sup>2)</sup> Ibidem 31 (1898), 2067.

<sup>3)</sup> Liebig's Annalen 302 (1898), 371.

<sup>4)</sup> The capital letters indicate the optical rotation of the original product, the small ones that of the final product. D-l-fenchylalcohol therefore is the laevogyrate alcohol obtained from dextrogyrate fenchene.

lævogyrate, provided that the reaction takes place at a low temperature. Upon the elimination of hydrochloric acid by means of aniline or chinoline, l-fenchene results. When the chloride, however, is submitted to different operations, as for instance to repeated distillation, or when the temperature at its formation was a high one, the chloride is but very little lævogyrate, and yields, when acted upon by bases, a mixture of l- and d-fenchene which is optically inactive or dextrogyrate. L-fenchene, more readily obtained, cannot be converted into d-fenchene, while this is converted into the lævogyrate hydrocarbon, when heated with alcoholic sulfuric acid.

D-l-fenchene is only slowly acted upon when oxidized by means of potassium permanganate solution, being converted into D-l-oxyfenchenic acid, melting at  $152^{\circ}$  to  $153^{\circ}$ , while D-d-fenchene is readily oxidized into D-d-oxyfenchenic acid, melting at  $138^{\circ}$  to  $139^{\circ}$ . From a mixture of the two fenchenes the pure lævogyrate hydrocarbon, therefore, can be obtained by fractionate oxidation by means of permanganate solution. d-fenchene can also be converted into l-fenchene by decomposition of the fenchylchloride, which is formed when a solution of d-fenchene in glacial acetic acid is acted upon by hydrochloric acid.

d-fenchylalcohol, obtained from l-fenchone (L-d-fenchylalcohol), shows a similar behavior as l-fenchylalcohol when converted into its chloride; the fenchene resulting therefrom by elimination of hydrochloric acid yields L-d-oxyfenchenic acid, melting at  $152^{\circ}$  to  $153^{\circ}$ , when acted upon by alcoholic solution of sulfuric acid and subsequently oxidized by permanganate solution. Equal parts of D-l- and of L-d-oxyfenchenic acid yield a racemic mixture with a lower melting point than each of its component parts has.

D-d-oxyfenchenic acid, when oxidized in acid solution yields, like D-l-oxyfenchenic acid (see our Report, October 1898, p. 48), a fenchocamphorone  $C_9H_{14}O$ , which differs from that obtained from D-l-oxyfenchenic acid by melting at  $62^{\circ}$  to  $63^{\circ}$  and being lævogyrate. Both ketones render oximes and semicarbazones, differing not only in their melting points, but also in their optical rotation.

Prof. Wallach's observations indicate that d- and l-fenchene are two hydrocarbons physically isomeric, with one double linking; their behavior with permanganate solution admits the inference that double linkings with stereoisomeric compounds can more or less readily be disassociated.

The sesquiterpenes seem more recently to have engaged the interest of various investigators. A more comprehensive examination of these hydrocarbons, heretofore somewhat neglected, would be very desirable; the only ones thus far determined are cadinene, caryophyllene and perhaps humulene. Of course, many difficulties

will have to be surmounted in this work and it will require much time before a classification of the sesquiterpenes similar to that of the terpenes will be attained.

Prof. Edw. Kremers<sup>1)</sup> has made a comparative examination of caryophyllene and humulene, and has shown these hydrocarbons, so similar in their physical properties, to differ in the melting points of their derivatives so much that they by no means can be considered to be identical. The differences observed are plainly shown by the following figures:—

	Caryophyllene	Humulene		Caryophyllene	Humulene
$d_{20}^0$	= 0.9032	0.8977	Nitrosite	m. p. 107 <sup>0</sup>	120 <sup>0</sup> -121 <sup>0</sup>
$n_D$	= 1.50019	1.50094	Isonitrosite	„ „ 53 <sup>0</sup> -56 <sup>0</sup>	165 <sup>0</sup> -168 <sup>0</sup>
$[\alpha]_D$	= —8 <sup>0</sup> 74'	—0.5 <sup>0</sup>	Nitrolbenzylamine	„ „ 125 <sup>0</sup> -128 <sup>0</sup>	136 <sup>0</sup>
Nitrosochloride m. p.	158 <sup>0</sup> -160 <sup>0</sup>	164 <sup>0</sup> -165 <sup>0</sup>	Nitrolpiperidine	„ „ 141 <sup>0</sup> -142 <sup>0</sup>	153 <sup>0</sup>
Nitrosate	„ „ 147 <sup>0</sup> -150 <sup>0</sup>	162 <sup>0</sup> -163 <sup>0</sup>			

It has also been shown that the nitrosate of caryophyllene, when boiled with alcoholic alkali, is converted into a compound crystallizing in needles and melting at 220° to 223°, which appears to be an oxime.

Mr. Brochet<sup>2)</sup> has investigated the action of formaldehyde upon menthol and borneol; he found that these two alcohols also readily act upon formaldehyde in the presence of sulfuric or hydrochloric acids, forming acetals. Dimethylmethylenacetale,  $\text{CH}_2(\text{O} \cdot \text{C}_{10}\text{H}_{19})_2$ , forms long silky needles melting at 56.5°; the corresponding compound of borneol,  $\text{CH}_2(\text{O} \cdot \text{C}_{10}\text{H}_{17})_2$ , has an odor similar to that of borneol and crystallizes in mother of pearl like shining lamellæ, melting at 166°. Both compounds withstand decomposition when heated in water or soda solution to 150° in a closed tube.

Linalool and geraniol do not render corresponding acetals.

Mr. J. Godlewsky<sup>3)</sup> has obtained from French oil of turpentine, by the action of alcoholic sulfuric acid according to the method of Mr. Flawitzky, a crystallizing, optically active terpeneol, which melts at 34° and has the opt. rotation of  $[\alpha]_D = -95.28^\circ$ . When this is converted into trioxymenthane,  $\text{C}_{10}\text{H}_{20}\text{O}_3$ , and this again is oxidized by chromic acid solution, a ketolactone,  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , is formed, which differs by its optical activity and a considerably lower melting point (45° to 46°) from methoethylheptanonolide obtained from inactive terpeneol (melting point 63° to 64°). This is very likely identical with the optically active ketolactone obtained in a different way by A. v. Baeyer and Baumgaertel<sup>4)</sup>.

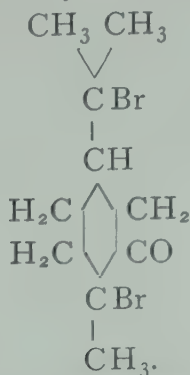
<sup>1)</sup> Pharm. Arch. 1 (1898), 211.

<sup>2)</sup> Compt. rend. 128 (1899), 612.

<sup>3)</sup> Chem. Ztg. 22 (1898), 827 and 23 (1899), 250.

<sup>4)</sup> Berichte d. deutsch. chem. Ges. 31 (1898), 3208.

These authors started from the optically active 1.8-dibromotetrahydrocarvone discovered by Wallach



In this compound the bromine atoms can be replaced one after another by the OH-group; by the replacement of only one bromine atom, oxybromotetrahydrocarvone, and of both, dioxytetrahydrocarvone or ketoterpin are formed. Both these compounds also are optically active. Upon the disengagement of hydrogen bromide from oxybromotetrahydrocarvone, oxycaron is formed and this is also converted into ketoterpin by breaking up the caron-ring by hydrolysis. This substance is reduced in alcoholic solution by metallic sodium into optically active 1, 2, 8-trioxyterpane, which again is converted by oxidation by means of chromic acid solution according to Wallach's statement into the optically active methylketone of the homoterpenylic acid, ketolactone  $\text{C}_{10}\text{H}_{16}\text{O}_3$ . This (see Godlewsky's statement on the preceding page), as well as trioxyterpan, differs from the compounds originating from inactive terpineol by a considerably lower melting point.

		active	inactive
Trioxyterpan . .	melting point	97° to 98°	121° to 122°
Ketolactone . .	„ „	48° „ 49°	62° „ 63°.

Pulegone has recently been found by Mr. F. M. Gage to be contained in the oil of *Mentha canadensis* L., and by Mr. F. Walden in the oil of *Pycnanthemum lanceolatum* Pursh. (*P. lanceolatum* and *P. linifolium* Pursh. used to be considered identical and were described as *Thymus virginicus* L.)<sup>1)</sup>. For the detection of pulegone in these oils the bisnitroso compound, recommended by Professor v. Baeyer<sup>2)</sup> is well suited. The melting point of bisnitrosopulegone is, according to Mr. Gage's statement, 81.5°.

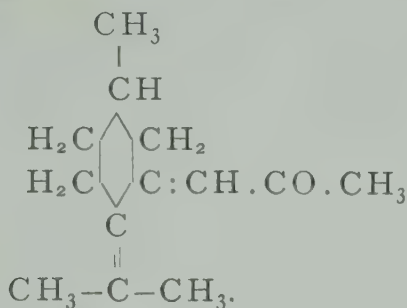
Mr. Barbier<sup>3)</sup> recently has described a condensation product of pulegone with acetyl acetic ester, which has the same composition

<sup>1)</sup> E. Kremers, Notes on two oils containing Pulegone. Pharm. Review 16 (1898), p. 412 and 414.

<sup>2)</sup> Berichte d. deutsch. chem. Ges. 28 (1895), 654.

<sup>3)</sup> Compt. rend. 127 (1898), 870.

as ionone,  $C_{13}H_{20}O$ , but not its violet odor. It is obtained by heating for some time a solution of equal molecules of pulegone and acetyl acetic ester in glacial acetic acid with fused chloride of zinc. The condensation product crystallizes from its solution in ligroïne in colorless prisms melting at  $72^\circ$  to  $73^\circ$ . Being a ketone, it forms with hydroxylamine an oxime,  $C_{13}H_{20}.NOH$ , melting at  $134^\circ$  to  $135^\circ$ . Mr. Barbier has named this ketone "pulegeneacetone", which very likely has the formula:—



Mr. Fromm<sup>1)</sup> has found in oil of savin an alcohol  $C_{10}H_{16}O$ , closely related to thujone (tanacetone), which the author terms "sabinol". By oxidation in the cold with a neutral saturated solution of potassium permanganate, this alcohol yields  $\alpha$ -tanacetogendicarboxylic acid  $C_9H_{14}O_4$  melting at  $141.5^\circ$ .

$\beta$ -tanacetogendicarboxylic acid  $C_9H_{14}O_4$ , melting at  $116^\circ$  to  $118^\circ$ , originating from  $\beta$ -tanacetketocarboxylic acid by action with bromine and sodium hydrate solution, renders, as is well known, dimethyl-laevulinic acid, when carefully oxidized by potassium permanganate<sup>2)</sup>. Messrs. Semmler and Tiemann<sup>3)</sup> at first called this acid  $\omega$ -dimethylaevulinic acid, but have changed this designation into  $\delta$ -dimethylaevulinic acid, since it has been found that this compound had been previously described by Professor Fittig, who obtained it from both  $\beta$ - $\gamma$ -isoheptenic acid and  $\beta$ - $\gamma$ -dibromoisheptenic acid. Pure  $\delta$ -dimethylaevulinic acid melts at  $42^\circ$  to  $43^\circ$ , its oxime at  $88^\circ$  to  $89^\circ$ .

Messrs. Semmler and Tiemann<sup>4)</sup> have published an investigation of carvenone,  $C_{10}H_{16}O$ , readily obtained by isomeration of dihydrocarvone by means of concentrated sulfuric acid. It was known that carvenone which, according to Mr. Bredt, is also contained in the so called "camphrene", obtained by action of sulfuric acid upon camphor, renders  $\alpha$ -methylglutaric acid as final product of oxidation. Messrs. Semmler and Tiemann have succeeded in

<sup>1)</sup> Vide Oil of savin, p. 41.

<sup>2)</sup> Berichte d. deutsch. chem. Ges. 30, (1897), 433.

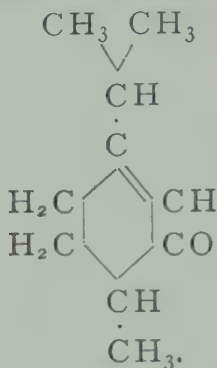
<sup>3)</sup> Ibidem 31 (1898), 2311.

<sup>4)</sup> Ibidem 31 (1898), 2889.

determining the intermediate products richer in carbon which are formed in the process of oxidation.

When carvenone is oxidized by a quantity of permanganate corresponding to 3 atoms of oxygen, from the glycol at first formed, by breaking up the ring, a two-basic oxyacid,  $C_{10}H_{18}O_5$  ( $\alpha$ -oxy- $\alpha$ -isopropyl- $\alpha_1$ -methyladipinic acid), melting at  $136^\circ$  to  $137^\circ$  is formed. Upon further oxidation by the elimination of  $CO_2$  this acid is converted into an oily ketonic acid,  $C_9H_{16}O_3$ . This is finally split up by the action of the oxidizer into acetone and  $\alpha$ -methylglutaric acid.

These transformations can well be explained by the formula of carvenone, already taken into consideration by Bredt:—



Carvenone used to be considered as having alcoholic character and in consequence had received the name of carveol by Professor A. v. Baeyer. When Professor Wallach proved it to be a ketone, he changed its name into carvenone. Although carvenone at present is generally recognized to be a ketone, Messrs. Marsh and Hart-ridge<sup>1)</sup> have recently described the same anew under the name of "carvenol"; they obtained it by the action of concentrated sulfuric acid upon camphor dichloride. Since, according to Mr. Bredt's observation, carvenone is contained in "camphrene", there can be no doubt that "carvenol" obtained from camphor dichloride is nothing else than carvenone. Carvenol yields upon reduction a saturated alcohol  $C_{10}H_{20}O$ , carvanol, which is converted by oxidation into the ketone  $C_{10}H_{18}O$ , carvanone. The properties of these compounds described by the authors are so completely those of tetrahydrocarveol and -carvone, that there cannot be any doubt about the identity of carvenol and carvenone. The authors nevertheless stick to their idea of denying their identity, maintaining the alcoholic character of the compound and the name of "carvenol" for the same.

Professor Wallach<sup>2)</sup> has published some further observations made on the carvone series. During the reduction of carvone a

<sup>1)</sup> Journ. chem. Soc. 73 (1898), 852.

<sup>2)</sup> Liebig's Annalen 305 (1899), 223.

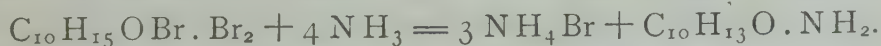
compound  $C_{20}H_{30}O_2$  is formed besides dihydrocarvone, which at first was considered to be a pinakone. According to recent observations verified by Messrs. Harries and Kaiser, this compound is a diketone named dicarvelone by Professor Wallach. The modification formed by the direct reduction of d- or l-carvone is called  $\alpha$ -modification; it is laevogyrate when obtained from d-carvone, dextrogyrate when obtained from l-carvone. Both compounds melt at  $148^\circ$ , while the melting point of the racemic mixture is at  $120^\circ$  to  $121^\circ$ .  $\alpha$ -Dicarvelone combines with two molecules of hydrogen bromide, the addition product yields, upon the elimination of the hydrogen bromide by means of alcoholic alkali, an isomeride of  $\alpha$ -dicarvelone,  $\beta$ -dicarvelone, melting at  $206^\circ$  to  $207^\circ$ . D- $\alpha$ -l-dicarvelone<sup>1)</sup>, when treated in the same way, yields a dextrogyrate, L- $\alpha$ -d-dicarvelone a laevogyrate isomeride; i- $\beta$ -dicarvelone melts already at  $168^\circ$ . Both  $\alpha$ - and  $\beta$ -dicarvelone are transformed by the action of concentrated sulfuric acid into a third isomeride,  $\gamma$ -dicarvelone, melting at  $126^\circ$ , whose racemic mixture also has a lower melting point ( $112^\circ$ ) than the active components.

When the hydrohalogen compounds of carvone are reduced by means of zinc dust and caustic soda, the halogen is not replaced by hydrogen, but disengagement of halogen hydrogen and the formation of eucarvone take place. Upon reduction, this yields more readily and abundantly dieucarvelones, corresponding to and identical with the dicarvelones.

In connection with these researches, Professor Wallach refers to his observations made when preparing eucarvone, eucarvoneoxime and dihydroeucarvylamine, which correspond to the results previously obtained by Professor A. v. Baeyer. He furthermore describes some new characteristic derivatives of dihydroeucarvylamine, among them urea, phenylurea and phenylthiourea, of which the latter seems to exist in various modifications.

The condensation of eucarvone with benzaldehyde by means of sodium ethylate renders a yellow, normal (melting point  $112^\circ$  to  $113^\circ$ ) condensation product, containing for 1 mol. of eucarvone 1 mol. of benzaldehyde, and a colorless abnormal (melting point  $193^\circ$  to  $194^\circ$ ) product, consisting of 1 mol. of eucarvone and 2 mols. of benzaldehyde. The latter probably belongs to the group of hydropyronic derivatives.

When ammonia gas is allowed to pass into an amylalcoholic solution of carvonetribromide, the following change takes place:—



The resulting fluid compound is a ketonic base, as may be proved by the preparation of an oxime. When set free from its hydrochloride by means of alkali, it separates in an oily form, but when

<sup>1)</sup> For an examination of these figures see note at fenchene on page 49.

left for some time in the fluid, it is converted under evolution of ammonia into a lactone  $C_{10}H_{14}O_2$ , carvenolide. The lactones obtained from optically active carvonetribromide are also optically active and melt at  $41^\circ$  to  $42^\circ$ , i-carvenolide obtained from i-carvone-tribromide melts at  $70^\circ$  to  $72^\circ$ . Carvenolide when boiled for some time with alcoholic alkali is converted into the unsaturated carvenolic acid  $C_{10}H_{16}O_3$ , when active melting at  $133^\circ$ , when inactive melting at  $135^\circ$  to  $136^\circ$ ; this acid has no tendency to form a lactone and its chemical constitution has not as yet been ascertained.

The opinion has been entertained since quite a time that the alcohols geraniol,  $C_{10}H_{18}O$ , and citronellol,  $C_{10}H_{20}O$ , are closely related to each other since both are often found to be contained at the same time in essential oils. As citronellol differs in its chemical composition from geraniol only by containing two more atoms of hydrogen, the inference was made that citronellol is dihydrogeraniol, but the transformation of geraniol into citronellol by the addition of hydrogen has thus far not been realized. This transformation, however, has been accomplished by the way of geranic acid, whose synthetic preparation is known since some time, so that citronellol now may also be prepared synthetically. But the price of the product would be a high one.

When an amylalcoholic solution of geranic acid is reduced by means of metallic sodium, it directly combines, according to Professor Tiemann's<sup>1)</sup> statement, with two atoms of hydrogen, being thereby converted into citronellic acid, which chemically is identical with the acid obtained from citronellic nitrile. When calcium citronellate is mixed with calcium formiate and submitted to dry distillation, citronellal is formed, this can be converted into citronellol by reduction by means of sodium amalgam in alcoholic solution.

The compounds thus obtained differ from the natural ones by their optical inactivity.

In our Report of October 1898, p. 60, we referred to a paper of Mr. Ph. Barbier<sup>2)</sup> describing the preparation of a new alcohol, dimethylheptenol  $C_9H_{18}O$ , by heating geraniol with alcoholic potassa. Upon the analysis of this substance performed in our research laboratory, we then expressed the opinion that this compound is not dimethylheptenol  $C_9H_{18}O$ , but the alcohol methylheptenol  $C_8H_{16}O$  corresponding to ordinary methylheptenone.

Professor Tiemann<sup>3)</sup> has recently ascertained that, when geraniol is heated for some time with alcoholic potassa, methylheptenol  $C_8H_{16}O$  is formed, and not dimethylheptenol  $C_9H_{18}O$ .

<sup>1)</sup> Berichte d. deutsch. chem. Ges. 31 (1898), 2899.

<sup>2)</sup> Compt. rend. 126, 1423,

<sup>3)</sup> Berichte d. deutsch. chem. Ges. 31, 2989.

This was proved by analysis as well as by comparing the properties of the resulting alcohol with those of the methylheptenol previously prepared by Messrs. Wallach and Tiemann and Semmler. Methylheptenol boils at 85° to 86° under 15 Mm. pressure, under common atmospheric pressure at 175° to 176°. While geraniol when heated with alcoholic potassa yields a considerable amount of methylheptenol, the isomeric linalool remains almost unchanged when treated in the same way.

Mr. Barbier<sup>1)</sup> persists in his previous statements in regard to the formation of dimethylheptenol from geraniol; he prepared synthetically dimethylheptenol by the action of methyl iodide upon methylheptenone in the presence of magnesium; this product is said by Mr. Barbier to so completely correspond in all its properties to the alcohol obtained by the action of alcoholic potassa upon geraniol that there cannot be any doubt about the identity of both compounds.

Messrs. Flatau and Labbé<sup>2)</sup> have furnished a method for the separation of citral from citronellal which depends upon the fact that the aqueous solution of the sodium bisulfite compound of citral<sup>3)</sup> renders no precipitate with barium salts, while the insoluble barium bisulfite of citronellal is quantitatively precipitated. The separation of a mixture of both aldehydes is effected in the following way: At first the normal sodium bisulfite compound of the aldehydes is prepared and dissolved in water; this is precipitated by barium chloride and the precipitate of the citronellal compound is collected upon a filter. From the filtrate the citral is isolated by the addition of alkali and by shaking the fluid with ether. The barium sulfite compound of citronellal is agitated with alcoholic potassa avoiding heating, and is separated by filtration from the barium- and potassium sulfites formed. In order to remove the excess of alkali, the filtrate is saturated with carbonic acid gas, once more filtered, and the citronellal separated from the solution by the addition of water taken up by ether. By means of this method, Mr. Labbé<sup>4)</sup> has succeeded in obtaining besides 70 per cent. of citral 6 per cent. of citronellal from oil of lemongrass. In the same way citronella oil was found to contain 25 to 30 per cent. of citronellal and 2 to 5 per cent. of citral<sup>5)</sup>.

<sup>1)</sup> Compt. rend. 128, 110.

<sup>2)</sup> Bull. soc. chim. (III), 19, 1012.

<sup>3)</sup> The authors emphasize the fact that this compound contains citral and sulfurous acid, forming a radical which acts like an acid. The normal sodium bisulfite compound therefore seems not to come into consideration, but probably the compound called by Professor Tiemann "labile citraldihydrodisulfonate of sodium".

<sup>4)</sup> Bull. soc. chim. (III), 21, 77.

<sup>5)</sup> Flatau, Bull. soc. chim. (III), 21, 159.

According to statements of Mr. W. Stiehl, referred to in our Report, October 1898, pp. 57 to 59, lemongrass oil is said to contain at least three different isomeric aldehydes  $C_{10}H_{16}O$ , namely citral, citriodoraldehyde and allolemonal, differing in their behavior towards sodium bisulfite. This statement standing in contrast with all former ones has induced several chemists to again make investigations about lemongrass oil and citral, of which we append the following brief report.

Prof. F. W. Semmler<sup>1)</sup> states that the citriodoraldehyde of Stiehl when acted upon by an excess of sodium bisulfite is completely converted into the true sulfonic acid compound not acted upon by alkalis, which according to Stiehl is characteristic of citral (geranial). Since the  $\beta$ -naphthocinchonic acids of geranial and of the citriodoraldehyde, supposed to be different, have the same melting point  $200^\circ$ , there cannot be any doubt about the identity of the two aldehydes. Stiehl's allolemonal is according to Semmler a mixture of geranial (citral) with non-aldehydic optically active substances.

In a rejoinder Mr. Stiehl<sup>2)</sup> upholds his statements, claiming that the aldehydes citriodoral and allolemonal are converted into geranial (citral) when agitated with acid reagents, among them bisulfite solutions which contain free sulfurous acid, while geranial (citral), on the other hand, is converted into citriodoral by the action of alkalis and of salts containing weak acids. Therefore, geranial (citral) is stable in acid menstrua and citriodoral in alkaline ones only<sup>3)</sup>.

Mr. Stiehl is of the opinion that the oils of lemongrass, of lemon and others do not contain geranial (citral) but citriodoral and allolemonal only and that these are converted into citral by the action of bisulfite.

Prof. O. Doebner<sup>4)</sup> on the other hand, after recent researches, came to the conclusion that citral (geranial) is the only aldehyde contained to a considerable amount in oil of lemongrass. He prepared, closely following Stiehl's method, "citriodoral" and "allolemonal", and found that the  $\beta$ -naphthocinchonic acid obtained from each, melts at  $197^\circ$  to  $198^\circ$ , thus showing this acid to be identical with citryl- $\beta$ -naphthocinchonic acid previously described. Mr. Doebner has also examined preparations made by Mr. Stiehl. He obtained from "citriodoraldehyde" by the action of  $\beta$ -naphthylamine and pyruvic acid the well known citryl- $\beta$ -naphthocinchonic acid, melting at  $197^\circ$  to  $198^\circ$ , "allolemonal" proved to be a mixture of about equal parts of aldehydic and of non-aldehydic compounds. The aldehyde isolated from this mixture by sodium bisulfite also yielded citryl- $\beta$ -naphthocinchonic acid, melting at  $198^\circ$  to  $199^\circ$ . When crude

<sup>1)</sup> Berichte d. deutsch. chem. Ges. 31, 3001.

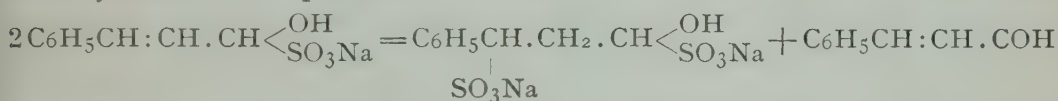
<sup>2)</sup> Chemiker-Zeitung 1898. II. 1086.

<sup>3)</sup> If this is correct, geranial (citral) could not be prepared in the usual way, since alkaline hydrates or carbonates are always used for its elimination from the bisulfite compound.

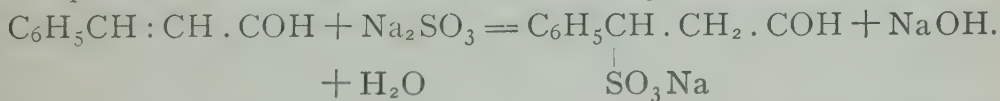
<sup>4)</sup> Berichte d. deutsch. chem. Ges. 31, 3195.

“allolemonal” was submitted to the action of  $\beta$ -naphthylamine and pyruvic acid, a mixture of  $\beta$ -naphthocinchonic acids, melting at  $210^\circ$  to  $235^\circ$  was obtained, from which pure citryl- $\beta$ -naphthocinchonic acid was obtained by extracting with glacial acetic acid. The residue, melting at  $225^\circ$  to  $235^\circ$ , consisted mainly of methyl- $\beta$ -naphthocinchonic acid.

Prof. Tiemann<sup>1)</sup> has also inquired into this controversy. In his paper he at first gives a sketch of the history of citral and then describes<sup>2)</sup> the hydrosulfonic acid derivatives of cinnamic aldehyde, of citronellal and of citral. Since some time it is known that many organic compounds containing double linkings add the elements of sulfurous acid, forming sulfonic acids. This reaction occurs readily with unsaturated aldehydes, for instance with acroleïne, crotonaldehyde &c. The behavior of cinnamic aldehyde with sulfites was studied by Mr. Heusler<sup>3)</sup> in 1891. When this aldehyde is agitated with sodium bisulfite, the normal, very little soluble double compound is at first formed, which when boiled with water decomposes in conformity with the equation:—



forming cinnamic aldehyde and the sodium bisulfite compound of hydrocinnamic aldehyde sulfonic acid. The latter is easily soluble in water, it is not decomposed by soda, but readily by alkaline hydrates. These statements were confirmed by Prof. Tiemann and his co-laborers; they found that the formation of the above mentioned hydrosulfonic acid is more easily accomplished, when neutral sulfites are used in place of acid ones and carbonic or acetic acids are employed for the neutralization of the alkali formed. The hydrosulfonic acid also is formed when cinnamic aldehyde is agitated with a solution of sodium sulfite and sodium bicarbonate. The reaction takes place in accordance with the following formula:



Since the resulting alkali, in a certain concentration, exercises a decomposing reaction upon the sulfonic acid formed, it has to be neutralized by acids.

Citronellal behaves in a similar way as cinnamic aldehyde; it yields with sodium bisulfite, besides the normal double compound



which can readily be decomposed by soda into its components, and

1) Berichte d. deutsch. chem. Ges. 31, 3278.

2) Ibidem 31, 3297.

3) Ibidem 24, 1805.

a hydrosulfonic acid derivative,  $C_9H_{18}(SO_3Na)COH$ , and its bisulfite compound. From the latter two compounds, the aldehyde can not be regenerated, neither by soda, nor by alkaline hydrates.

Of special interest is the behavior of citral with sulfites. Prof. Tiemann has succeeded in isolating three different hydrosulfonic acid derivatives of citral, besides the normal bisulfite compound.

The normal, bisulfite compound little soluble in water is best prepared by means of sodium bisulfite, containing some free acid, which can be accomplished by the addition of some acetic acid. The pure compound is partially decomposed by warming it with water, but can be recrystallized from the acid mother liquor, wherein it originated. A better way for purifying the compound consists in its recrystallization from acidulated methylic alcohol. It is decomposed by soda without however completely regenerating the citral, because in this process a small amount of a hydrosulfonic acid derivative is formed.

When the normal sodium bisulfite compound is taken up by water and submitted to steam distillation, half of the citral contained therein passes over, the balance is mostly converted into the sodium salt of the so-called "stable" citraldihydrodisulfonic acid:—



This compound is readily soluble in water without regeneration of the citral from the solution either by sodium carbonate or hydrate. Phenylhydrazine is readily taken up, which admits the inference that the compound still contains the aldehyde group  $COH$ .

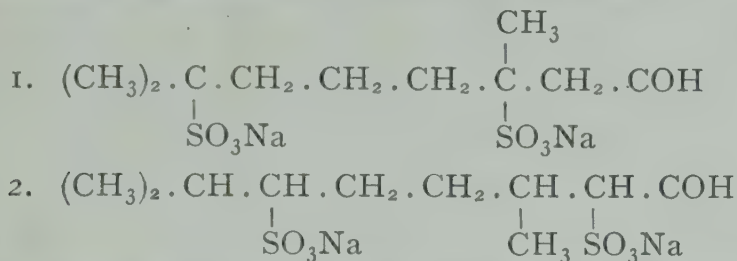
When citral is agitated with an aqueous solution of neutral sodium sulfite, the sodium salt of the "labile" citraldihydrodisulfonic acid results according to the following equation:—



This differs from the isomeric "stable" compound in being quantitatively decomposed by the action of sodium hydrate into citral and neutral sodium sulfite. As the preceding equation indicates, sodium hydrate also results at the formation of the labile citraldihydrodisulfonic salt, and as the former decomposes the sulfonic acid salt in a moderate concentration, the reaction can only be accomplished if the alkali, as soon as it is formed, is neutralized by the introduction of a current of carbonic acid or by a gradual and careful addition of dilute acetic or sulfuric acid. Another way to attain to the same result consists in adding at once to the sodium sulfite solution an amount of some acid salt, for instance sodium bicarbonate or sodium bisulfite, sufficient to neutralize the alkali that is formed. When citral is shaken with a solution of sodium bisulfite, containing neutral sodium sulfite, the labile dihydrodisulfonic salt is always formed, because the alkali set free combines with the bisulfite present, forming neutral sulfite, which

again reacts in the same way with the citral. These reactions offer a ready explanation of the rise of the "labile" compound whenever lemongrass oil is acted upon by a commercial sodium bisulfite solution, as had been observed by Mr. Dodge some years ago.

This labile sodium citraldihydrodisulfonate, obtained in a pure state and analyzed by Prof. Tiemann, renders a semicarbazone, when acted upon by semicarbazide. This admits the inference that this compound also contains the aldehyde group COH. The isomery of the same with the stable compound may be caused by differences in their structural agglomeration, perhaps in this way:—



Labile sodium citraldihydrodisulfonate takes up when shaken with citral a large quantity of this aldehyde, forming a citralmono-hydrosulfonic salt,  $\text{C}_9\text{H}_{16}(\text{SO}_3\text{Na})\text{COH}$ , which compound also is decomposed by alkaline hydrate while citral is regenerated.

Prof. Tiemann has ascertained that preparations of citral of different origin and methods of preparation show a uniform behavior towards sulfites; from each one of these preparations the one or the other of the hydrosulfonic derivatives described may be obtained at will.

Citral obtained by decomposition of the labile mono- and dihydrosulfonates is undoubtedly identical with the aldehyde regenerated from the normal sodium bisulfite compound, as may be seen from the following figures:—

	Citral obtained from the sodium sulfite compound	Citral obtained from sodium dihydrodisulfonate
Boiling point (20 Mm. pressure)	117° to 120°	117° to 120°
specific gravity at 20°	0.8890	0.8894
$n_D$ at 20°	1.4884	1.4881
$\beta$ -naphthocinchonic acid, m. p.	199° to 200°	199° to 200°
Semicarbazone (crude) „ „	135°	135°
„ (recrystallized) „ „	171°	171°

In a further publication Prof. Tiemann<sup>1)</sup> speaks of the qualitative and quantitative determination of citral. For its detection Doebner's reaction is generally used, converting citral by the action of pyrouvic acid and  $\beta$ -naphthylamine into citryl- $\beta$ -naphthocinchonic acid, which after recrystallisation melts at 200°. This reaction gives reliable results only when citral is present in an excess; when pyrouvic acid predominates, a secondary reaction takes place, which

<sup>1)</sup> Berichte d. deutsch. chem. Ges. 31, 3324.

among other products yields methyl- $\beta$ -naphthocinchonic acid, melting at  $310^{\circ}$ ; this is much less soluble in alcohol and glacial acetic acid than the citryl compound, of which property use may be made for the preparation of the pure citrylic compound from such a mixture of naphthocinchonic acids.

By condensation of citral with cyan-acetic acid, a citralidene cyanacetic acid  $C_9H_{15} \cdot CH : C \begin{smallmatrix} \text{CN} \\ \text{COOH} \end{smallmatrix}$  is formed which crystallizes in fine crystals and melts at  $122^{\circ}$ . This compound also is very well adapted for the detection and for the approximate quantitative determination of citral in essential oils. The behavior of citral towards semicarbazide has also been used for the detection of the aldehyde, without, however, giving a satisfactory result, because mixtures of semicarbazones with different melting points ( $130^{\circ}$  to  $170^{\circ}$ ) are formed. Messrs. Barbier and Bouveault supposed they had obtained from such a mixture three isomeric semicarbazones melting respectively at  $130^{\circ}$ ,  $160^{\circ}$  and  $171^{\circ}$ , corresponding to three structural-isomeric citrals. Later on they supposed the semicarbazones melting at  $135^{\circ}$  and  $171^{\circ}$  to belong to two stereoisomeric aldehydes  $C_{10}H_{16}O$ .

Mr. G. Lemme obtained a semicarbazone crystallizing in needles and melting at  $164^{\circ}$  by the action of a solution of semicarbazide hydrochloride in glacial acetic acid upon citral, without adding sodium acetate. At this reaction, the semicarbazone melting at  $164^{\circ}$  is freely formed and separated. The remaining mother liquors yield the semicarbazone melting at  $171^{\circ}$  and crystallizing in lamellæ. A mixture of both semicarbazones melts at  $135^{\circ}$ . On the other hand, the formerly observed semicarbazone melting at  $135^{\circ}$  yielded by repeated crystallizations the semicarbazone melting at  $171^{\circ}$ . From this fact Prof. Tiemann inferred that by the action of the semicarbazide upon citral only the two semicarbazones melting at  $164^{\circ}$  and  $171^{\circ}$  are formed.

Prof. Tiemann has made these reactions with various citral preparations, obtained partly from lemongrass oil, partly by oxidation of linalool and geraniol, always getting the same reaction products, so that the identity of the aldehydes of the different preparations seems to be doubtless.

For the quantitative determination of citral in lemongrass oil the use of indirect methods deserves the preference. The aldehyde is converted into the normal, little soluble sodium bisulfite compound by agitating the oil with sodium bisulfite solution containing acetic acid, or, by the action of an alkaline solution of sodium cyanacetate, into the readily soluble sodium citralidene cyanacetate, or also, by the action of sodium sulfite and sodium bicarbonate, into the labile sodium citraldihydrodisulfonate. The non-aldehydic compounds are separated from the citral-derivatives formed by agitation with ether and are weighed after the evaporation of the solvent. The difference between the weight of the oil used for the determination and the

weight of the non-aldehydes represents the amount of citral contained in the oil.

Prof. Tiemann<sup>1)</sup> furthermore has studied the action of alkaline and acid agents upon citral with a view to find out whether it is possible to obtain in this way structural-isomeric aldehydes by displacing the double linkings.

Citral becomes completely resinified by the action of alcoholic potassium hydrate, and, as Mr. Verley has shown, it is resolved into methylheptenone and acetaldehyde upon being boiled with a solution of alkaline carbonates. When it was agitated for one hour with a 5 percent. sodium hydrate solution, Tiemann obtained a product yielding 23 per cent. of a resinous substance with the odor of methylheptenone and 77 per cent. of citral; the latter is characterized by citryl- $\beta$ -naphthocinchonic acid, melting at 199° to 200°, and by citralidene cyanacetic acid, melting at 122°.

It is known since years that citral is subjected to great changes, forming cymol when acted upon by acid agents; the nature of the intermediate products formed is not known. It remained, therefore, to ascertain whether in this process migrations of the double linkings occur, such as take place at the transformation of linalool into geraniol when acted upon by acetic anhydride. Prof. Tiemann has made experiments in this direction by allowing sulfurous acid, sulfuric acid of a 10 per cent. strength, and a chromic acid mixture to act upon the aldehyde. In every case a more or less considerable resinification took place with the simultaneous formation of cymol, but never an isomerization. From the products of the reaction there could be regenerated in every case the well known citral with its characteristic properties.

Another investigation of Prof. Tiemann<sup>2)</sup> concerns the behavior of citral towards semicarbazide. When they are allowed to act upon one another, two isomeric semicarbazones, melting at 164° and 171° are formed, as already mentioned. It remained to investigate whether the isomery of these semicarbazones depends upon the fact that they correspond to two stereo-isomeric forms of citral. Experiments made are supporting this view. When the normal sodium bisulfite compound is mixed with water, sodium carbonate being added, and is then shaken with ether, about one half of the aldehyde passes into the ether (fraction a); the remainder is separated from the mother liquor by the action of sodium hydrate, and is subsequently also taken up by ether (fraction b). Both fractions have the same physical properties but act differently with semicarbazide, since fraction a yields only the semicarbazone, melting at 164°, and fraction b a mixture of both semicarbazones, melting at 164° and 171°. With cyanacetic acid, fraction a yields only citral-

<sup>1)</sup> Berichte d. deutsch. chem. Ges. 32, 107.

<sup>2)</sup> Ibidem 32, 115.

idene cyanacetic acid, melting at  $122^{\circ}$ . From the derivative of cyanacetic acid obtained with fraction b, a small amount of an acid melting at  $80^{\circ}$  could be isolated.

Whether this really indicates stereo-isomerous forms of citral remains to be decided by further researches.

Mr. Labbé<sup>1)</sup> has isolated from oil of lemongrass by means of the barium bisulfite compound 7 to 8 per cent. of citronellal and 76 to 77 per cent. of citral; besides these, small amounts of methylheptenone and of geraniol were found in the oil and it very likely<sup>2)</sup> contains also capronic and caprinic acids, probably in the form of geraniol esters. According to Mr. Flatau<sup>3)</sup> the citral obtained by oxidation from pure geraniol gives a mixture of semicarbazones, but he thinks that this is not due to the presence of different aldehydes.

The preceding reports indicate that oil of lemongrass contains only one aldehyde of the formula  $C_{10}H_{16}O$ , the well known citral; this possibly may exist in two stereo-isomerous forms. Citral is characterized by the citryl- $\beta$ -naphthocinchonic acid, melting at  $199^{\circ}$  to  $200^{\circ}$ , and the citralidene cyanacetic acid, melting at  $122^{\circ}$ . It yields with alkaline sulfites, besides the normal bisulfite compound, soluble hydro-sulfonic acid derivatives, which are decomposed by sodium hydrate with regeneration of citral (labile compounds), or else are stable (stable compounds).

We also have entered upon an investigation of lemongrass oil and in conclusion add a brief report, although our researches are not yet completed. We have prepared the aldehyde of lemongrass oil by treating the oil with acidulated sodium bisulfite solution and subsequent decomposition of the normal sodium bisulfite compound by means of soda, as also by shaking the oil with a solution of sodium sulfite and sodium bicarbonate and subsequent decomposition of the labile sodium citral dihydrodisulfonate by means of sodium hydrate. Both methods furnished fully identical products of citral.

	Citral made with acid sodium bisulfite.	Citral made from the alkaline solution of hydrosulfonic acid.
Boiling point 12 Mm.	$110^{\circ}$ to $111^{\circ}$	$110^{\circ}$ to $111^{\circ}$
$\alpha_D$	$\pm 0^{\circ}$	$\pm 0^{\circ}$
$n_D$ at $17^{\circ}$	1.49015	1.49015
sp. gr. at $15^{\circ}$	0.8932	0.8930
$\beta$ -naphthocinchonic acid m. p.	$200^{\circ}$ to $201^{\circ}$	$200^{\circ}$ to $201^{\circ}$ .

We could not in any way obtain from the oil an optically active aldehyde, while we succeeded in finding about 1 per cent. or less of aldehydes of the fatty acid series. They probably are due to the presence of caprinealdehyde and lower homologues of the same,

<sup>1)</sup> Bull. soc. chim. III, 21 (1899), 77.

<sup>2)</sup> Ibidem 21 (1899) 159.

<sup>3)</sup> Ibidem 158.

because the presence of capric acid melting at  $31^{\circ}$  could be demonstrated in the mixture of acids resulting from the oxidation of the aldehydes.

The presence of methylheptenone in lemongrass oil, readily to be noticed by its odor, can be shown by submitting the oil to fractionate distillation and by shaking the fraction passing over at  $180^{\circ}$  with sodium bisulfite. The methylheptenone disengaged from the solid bisulfite compound by means of soda shows the following properties:

Boiling point	$173^{\circ}$ ,
sp. gr. at $15^{\circ}$	0.855,
$n_D$ at $20^{\circ}$	1.43805,
$\alpha_D$	$\pm 0^{\circ}$ .
Semicarbazone melting point	$136^{\circ}$ to $137^{\circ}$ .

The amount of methylheptenone contained in oil of lemongrass is 1 to 2 per cent.

For years we have manufactured geraniol from the residues remaining in the preparation of citral. For ascertaining that geraniol is not produced by the reducing influence of the sodium bisulfite upon citral, but is really a component part of the oil, we have made use of the following method: Lemongrass oil was heated for some time on a water-bath with benzoic acid anhydride, the volatile portions (citral) were then removed by steam and the less volatile remainder was boiled with alcoholic alkali in order to decompose the benzoic acid ester formed. After the evaporation of the alcohol, the residue was re-distilled with steam, the oily distillate converted into the calcium chloride compound and this purified and subsequently decomposed by water. The geraniol obtained had the following constants:—

Boiling point	$229^{\circ}$ to $230^{\circ}$
specific gravity at $15^{\circ}$	0.8808
$n_D$ at $17^{\circ}$	1.47665
$\alpha_D$	$\pm 0^{\circ}$
Diphenylurethane, melting point	$82^{\circ}$ .

The amount of geraniol contained in lemongrass oil is 4 to 6 per cent. It seems, however, to contain still more of the alcohol in the form of esters.

The method published and recommended by us in 1891 for the determination of the cinnamic aldehyde in cassia oil, serves us also for the quantitative estimation of citral in oil of lemongrass. Into a "Schimmel's cassia oil flask" having a capacity of about 100 Cc., whose neck has a length of 130 Mm. and a width of 8 Mm. and has a scale graduated in tenths of a cubic centimeter, 10 Cc. of lemongrass oil are brought. To this oil is gradually added, with constant agitation, a solution of sodium bisulfite until this ceases to act upon the oil;

the reaction is completed by heating the flask upon the water-bath. After cooling, so much water or bisulfite solution is added as is needed to force the remaining uncombined oil into the neck of the flask, where its volume is exactly indicated by the scale. This oil represents the non-aldehydic constituents of lemongrass oil. Its volume subtracted from the 10 Cc. of the oil used indicates the amount of citral contained in the oil. We have employed this method for years and found that the percentage of citral contained in oil of lemongrass ranges between 75 and 83.

**Citral.** The consumption of this product has become a very considerable one, mainly for the preparation of concentrated oil of lemon. The natural lemon oil contains on the average  $7\frac{1}{2}$  per cent. of citral. If for instance 75 Gm. of citral are added to 925 Gm. of oil of lemon, the resulting 1 kilo of oil has double the strength of normal oil of lemon. It is advisable to make oil of lemon the basis of these concentrated citral preparations, because they thereby receive a fresher aroma; such mixtures are specially adapted for making sirup for lemonades, for soda-water &c., because a smaller quantity of the flavor is used and a clearer sirup is obtained. Of the mixture made in the proportions just stated, 20 to 25 Gm. would be sufficient to flavor 100 kilos of sirup, and 10 to 15 Gm., when the mixture is made with double the quantity of citral.

**Cumarin.** Years ago we fully dwelled upon the subject of the solubility of cumarin, because a correct knowledge in this regard is requisite for a practical use of this fine aroma. In compliance with constantly recurring inquiries of old as well as of new customers, we deem it useful to repeat the information previously given:—

100 parts of alcohol	at 0° C.	at 16 to 17° C.	at 29 to 30° C.
of 90 volume per cent. dissolve	7.1 parts	13.7 parts	42.5 parts
„ 80 „ „ „ „	6.0 „	12.3 „	38.3 „
„ 70 „ „ „ „	4.4 „	9.1 „	26.0 „
„ 60 „ „ „ „	3.2 „	6.0 „	16.0 „
„ 50 „ „ „ „	1.7 „	3.4 „	8.9 „
„ 40 „ „ „ „	0.7 „	1.5 „	3.9 „
„ 30 „ „ „ „	0.3 „	0.6 „	1.7 „
„ 20 „ „ „ „	0.2 „	0.4 „	0.8 „
„ 10 „ „ „ „	0.15 „	0.25 „	0.5 „
100 parts of water dissolve	0.12 parts	0.18 parts	0.27 parts.

In order to avoid any separation of cumarin from its solutions in consequence of a decrease of the temperature, it is advisable in the preparation of these solutions not fully to apply the maximum quantities of cumarin. If the quantity of cumarin soluble at 0° is taken as a standard, the possibility of any separation at common temperatures is excluded.

In place of the old-fashioned tonca-beans infusion, an alcoholic solution of cumarin should be employed. While the former infusion was prepared by employing

250 Gm. of tonca-beans to  
1 kilo of 90 per cent. alcohol,

it is completely and better replaced by a solution of

4 Gm. of cumarin in  
1 kilo of 90 per cent. alcohol.

The amount of cumarin contained in the best grades of tonca-beans is generally considered to be  $1\frac{1}{2}$  per cent.

**Eucalyptol.** A nostrum has recently appeared in the market under the name of "Cineol" which, as proved by an examination of the Carlsruhe Board of Health, consists of a mixture of the oils of turpentine, eucalyptus and cajeput. It is to be regretted that names of definite chemical compounds like cineol are misused in this way.

Combinations (?) of eucalyptol (cineol) with the naphtols, called  $\alpha$ - and  $\beta$ -eunol, are said to act as antiseptics and have recently been recommended for use in dermatology and surgery.

**Heliotropin.** Competition has successively cut down the price of this article to  $\mathcal{M}$  30.— per kilo and, as we are informed, even to  $\mathcal{M}$  26.—. The product offered at this price shows, however, less careful crystallization and seems not to be equal to the best grade of this commodity.

As the warm season is approaching, we do not fail to recall the fact that heliotropin must be protected against the influence of light and heat.

Molten heliotropin forming a brown fluid is useless to the perfumer; the crystals therefore should be kept in a cool and dark place during the summer months. A temperature of 30° C. having a destroying effect on its perfume, heliotropin should not be bought in large quantities during the hot season. Consumers residing in hot climates should upon the receipt of heliotropin dissolve it at once in alcohol and keep this solution in a cool and dark place in order to preserve the flavor unimpaired.

So-called amorphous heliotropin, consisting of a mixture of heliotropin and some vanillin with the inodorous and inert anisic acid, seems to have been withdrawn from the market since we exposed its composition in our Report of October 1893.

**Menthol, crystallized.** The price of this commodity has again been decreased by excessive production, especially after Japanese capitalists had in vain tried to monopolize the article. The higher quotations of German manufacturers are due entirely to differences in the quality of the article. We have not met with a cheaper menthol as pure and dry as ours, or even equalling it. It would be easy also to compete with cheaper grades but we prefer to adhere to our principle and to produce and supply the very best of this article too.

We prefer to refrain from any anticipation in regard to the impending price fluctuations of this commodity; the peculiar circumstances prevailing in Japan are apt to defy any conjectures.

**Safrol.** The use of this product as a perfume for domestic soaps, first introduced in the United States, meets with increasing favor in Europe, and other continents also. There is hardly any appropriate substance at so fair a price which has a relatively equal diffusive power for flavoring common soaps. The present value is in conformity with the ruling price of the raw material and there is no valid cause for an essential change of the present rates.

**Terpineol.** The issue of November 5<sup>th</sup> 1898 of the London Pharmaceutical Journal contains among other so-called "new remedies" a note said to be quoted from the "Centralblatt für Therapeutik", stating that terpineol is used in cases of bronchial enlargement. It is said to be prescribed in pills or capsules in the following recipe: Terpineol and sodium benzoate, each 1 Gm., sugar, a quantity sufficient for making 10 pills or capsules, of which one is to be taken every 1 or 2 hours. Another recipe is: Terpineol 0.1, sweet oil 0.30 to each gelatine capsule, one to be taken every 2 hours.

**Thymol, crystallized.** After having received the new shipments of Ajowan-seeds, we have adjusted our rates for thymol, and can supply any demand.

**Vanillin.** In our last Report we called attention to a sophisticated article, a mixture of vanillin and antifebrine. Our attention has recently been called to another similar product offered in Austria; this consists of 35.26 per cent. of vanillin and the balance of acetyl-isoeugenol. All this calls for the exercise of great discrimination in purchasing vanillin.

Schimmel & Co.

During the last six months the war on both hemispheres, followed by a permanent political crisis in East Asia, has not failed to exercise a detrimental effect upon the commercial intercourse especially with the nations directly engaged in the combat. The consequences will be felt for some time on both sides although there can be no doubt that a country so wealthy in natural resources as the United States will soon financially recover and even draw considerable profit from its recently acquired position in some of the most important colonies.

Notwithstanding the prompt and successful result of the war, the long hoped for general bussiness prosperity in the United States as yet has delayed to set in. The European and particularly the German industries and commerce cannot fail to sustain noticeable drawbacks as will soon be seen from general statistical export figures.

In our line of products the following figures already indicate a considerable decrease of the transactions with the United States.

Export of essential oils and fine chemicals during the fiscal year from July 1<sup>st</sup> 1896 to June 30<sup>th</sup> 1897:

1896	1896	1897	1897
July 1. to Sept. 30.	Octb. 1. to Dec. 31.	Jan. 1. to March 31.	April 1. to June 30.
\$ 72,092.83	\$ 107,181.28	\$ 129,863.19	\$ 92,569.37

The same during the fiscal year July 1<sup>st</sup> 1897 to June 30<sup>th</sup> 1898:

1897	1897	1898	1898
July 1. to Sept. 30.	Octb. 1. to Dec. 31.	Jan. 1. to March 31.	April 1. to June 30.
\$ 61,199.47	\$ 100,771.75	\$ 78,254.08	\$ 72,972.30

Total amount from July 1<sup>st</sup> 1896 to June 30<sup>th</sup> 1897 . . . \$ 401,700.67

" " " " 1<sup>st</sup> 1897 " " 30<sup>th</sup> 1898 . . . \$ 313,197.61

showing a decrease of \$ 88,509.06

The American War Tax Law of June 13<sup>th</sup> 1898 affects besides many imported goods a number of domestic products, of which those in our line are perfumeries, cosmetics, distilled aromatic waters, essences and oils in small parcels. The revenue stamp tax, however, is not excessive.

Trade with Cuba has again been resumed but will remain limited and unsettled for quite a time. For the present the custom-house formalities will be the same there as in the United States. This will equally be the case with the Philippine Islands.

If the pending controversies between the Argentine Republic and Chile should really culminate in the outbreak of hostilities, detrimental consequences would result for the German commerce with South America, both countries being of considerable importance to our industries.

In Costa Rica the gradual introduction of the gold standard was begun last year.

Transactions with Brazil still require discrimination and caution since domestic quiet and trust are still largely wanting. Values have recently somewhat rallied but confidence in their stability is still slight.

While, on the whole, the conditions and the prevailing state of affairs in the countries of the Western hemisphere are not particularly favorable and encouraging, those of the Eastern hemisphere fortunately are better settled and more propitious, with the exception of Spain which will suffer for an indefinite time from the consequences of an unfortunate war. Secure in the enjoyment of peace and blessed with abundant crops, Europe can count upon continued national prosperity and upon a steady development and growth of its industries and commerce.

The transition of Japan and Corea to the gold standard augurs well for the new era of solid progress in Eastern Asia.

The chemical industry of Germany and its superiority, as is well known and generally acknowledged, has obtained a powerful impetus and has much progressed in the course of recent years. The increase of its production may well be illustrated by the following authentic figures:—

	1882	1895	Increase :
Export in bulk :	471,218 tons	651,341 tons	38.2 per cent
Export in value : <i>M</i>	221,298,000.—	290,097,000.—	31.1 " "

Of some importance to a part of our customers and still more to the agricultural industry of Germany is the law issued July 6<sup>th</sup> of the present year protecting the sugar-beet growers against the competition by artificial sweetening products, forbidding their use for sweetening foods, beverages etc. This law was anticipated in Austria by a similar ordinance, issued April 20<sup>th</sup> 1898.

Little and nothing definite has transpired about the recent commercial treaty between Germany and Great Britain. The former terms still in force have been prolonged by the law of May 11<sup>th</sup> 1898 to remain valid till July 30<sup>th</sup> 1899.

The new German rail-road tariff with its reduced rates for single parcel goods, gone into effect October 1<sup>st</sup> 1898, is mainly directed against the practice of the collective despatch of freight. This departure is an advantageous one to customers in remoter localities who often depend for their supply upon the prompt transportation of smaller parcels. It is to be hoped that the benefit derived thereby will not be counteracted by a slower despatch, for rapid supply is an important factor in our age of haste and promptness.

The transfer of our Austrian branch from Prague to Bodenbach on the Elbe river, to which we briefly referred on page 4 of our last Report, was completed on the 1<sup>st</sup> of September of this year. Our new establishment adjoins both the rail-road depot and the steam-boat landing and is spacious enough and well appointed to accommodate all requirements of our constantly increasing business with Austro-Hungary.

Not only the crops of cereals, but also the various aromatic plants used in our industry, have been benefitted by the favorable weather prevailing in most of the European states from the middle of July until after the completion of the harvests. Only in some parts of southern France persistent drought has considerably impaired the crops of aromatic plants.

Much research and valuable studies have been carried on during the last six months in the interesting domain of essential oils and their constitution, and ample material for scientific reports has been gathered. In recording the most important and useful results in our semi-annual Reports, we aim at the greatest possible completeness, without, however, exceeding the proper limits of the periodical pamphlet, combining in commensurate union business and scientific records, both useful and instructive to every reader interested in our line of products.

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**Almond Oil, bitter, synthetical, free from chlorine.** Although our price lists contain the special statement that we guarantee our product to be free from chlorine, we take occasion once more to emphasize this fact and to predict that the price of this product may be further reduced in proportion to the increase of its use.

**Almond Oil, pressed from kernels.** The peach crop in Syria has been a normal one this year and cheap prices were to be expected. A brisk demand, however, set in, caused by speculators in

Marseilles who made an effort to corner the article. The rates are therefore rather higher than last year so that the price of the pressed oil will have to be raised.

The demand for true essential oil is so brisk, notwithstanding the competition of the two synthetic benzaldehydes, that we hardly are able to comply with the large orders.

We expect the first supplies of new kernels during October and have enlarged our facilities for pressing the oil.

**Almond Oil, pressed from sweet almonds.** The unusual rise of the price of sweet almonds in the course of this summer has induced us to discontinue for the time the pressing of this oil, because we are sure that it originated in artful speculation based upon false statements as to the amount of the stock of almonds. The fact is that only little transactions have taken place at so enormous rates; the prices of late have been on the decline, although they are still far from the former normal rate. The highest price prevailed in May, amounting to about *M.* 180.— per kilo, declining until August to *M.* 140.—. At present the rate is *M.* 145.— to *M.* 150.—

The yield and stock of Bari almonds amounted during the last two years as follows:

in 1896:	yield about	120,000 bales;	stock in	1897:	20,000 bales.
„ 1897:	„ „	60,000 „	„ „	March 30 <sup>th</sup> 1898:	10,000 „

The entire crop on the island of Chios, usually amounting to about 15,000 cwts. has proved a complete failure this year in consequence of persistent drought.

In order not any longer to disappoint our customers, we are again about to start the pressing of oil of sweet almonds; we beg, however, to extend the advise, to lay in only what is urgently needed as a further decline of prices is to be expected.

**Angelica Oil.** The yield of our Angelica plantations has been a normal one this year. The plants grew luxuriantly but the roots remained rather deficient in essential oil. For the first time this year we have allowed the fruits to ripen on a part of the plants and have distilled the fine Angelica-fruit oil. Although this is less profitable from an economic point of view, it tends to increase our independence from other markets, a problem the solution of which has been our constant aim.

**Angostura-bark Oil.** The investigation of this oil by Messrs. Beckurts and Troeger, reported in our Report of April 1898, p. 6, has meanwhile been completed<sup>1)</sup>. The laevogyrate sesquiterpene called galipene by the authors has proved to be identical with cadinene; they have, however, as yet not succeeded in ascertaining the con-

<sup>1)</sup> Archiv d. Pharm. vol. 236, pp. 392 to 408.

stitution of the so-called galipenic alcohol, now called galipol, of which the oil contains 13 to 14 per cent as is proved by the acetylation process. Besides, a small amount of a terpene  $C_{10}H_{16}$ , probably pinene, the oil also contains an inactive and but slightly characterized sesquiterpene for which the authors propose the name galipene.

**Anise Oil.** The recent anise crop in Russia was a so abundant one as to cause a considerable decline of prices. In consideration of this fact it was somewhat a surprise that the supply to the first anise market held in Krasnoje, September 12<sup>th</sup> was a relatively short one. The expected decline failed to set in. The purchases for Russian distillers were brisk while the principal dealers remained reluctant in purchasing, evidently preferring to take their chances until the second anise market, October 25<sup>th</sup>. Before this an approximate estimate of the total crop would be unavailing. The opinion, however, prevails that this may amount to considerably more than 5,000,000 kilos.

As a result of these favorable chances the prices of anise oil and of anethol have experienced quite a decline. According to our statistical records they have during the last 20 years never reached so low a rate as at present. In consequence a brisk business may be expected in these commodities.

According to Consular reports the anise production of some of the other principal anise furnishing countries has been for this year:

Anise-Export from Bulgaria in 1897 . .	402,463 kilos
"      "      "      "      " 1896 . .	667,072 "
"      "      " Chios " 1897 . .	500,000 "
"      "      "      "      " 1896 . .	400,000 "

The total production in Spain is estimated to amount to at least 800,000 kilos.

**Arnica-flower Oil,** since quite a time out of the market, could again be distilled this summer and is now in stock for ample supply.

**Cajeput Oil.** There is hardly any demand for this oil. The supply is inconsiderable, seems, however, to meet all demand. Four barrels containing about 700 kilos, and 399 bottles of oil, recently brought on the market in Holland did not find purchasers and may be offered at lower rates later on.

On account of its actual high price, oil of cajeput may well be replaced for technical application by eucalyptus oil of the genus *Globulus*, to which it nearly corresponds in its amount of cineol.

**Camphor Oil.** Since our last Report the price has constantly declined and may now again be considered a normal one. There

is hardly any chance for a return to the cheap prices governing this commodity for years in the European markets inasmuch as it has met with quite an extended application. Corresponding to a decrease in production, the export has experienced considerable decline. While the former amounted to 15,000 or 16,000 cases in 1886 and 1887, the export in 1897 reached little more than one half of this quantity.

The rectified white oil continues to find use in the European markets, as a substitute for oil of turpentine, for dissolving resins, caoutchouc etc., for cleansing machines and for "perfuming" the so-called soft turpentine soaps, now much used in various industries.

White light camphor oil has the advantage of less inflammability than others of the common solvents of resins. While, for instance, the flashing point of oil of turpentine is at  $33.7^{\circ}\text{C}$ ., that of light camphor oil is at  $44.5^{\circ}\text{C}$ .

**Cananga Oil** has recently become discredited in consequence of the constantly decreasing quality of the supplies. While the supply in Holland amounted to 2446 bottles in 1896, it was 449 bottles only in 1897. This turn necessitated a change of supply, which thus far has proved a success, inasmuch as the first shipment recently received, matches the former ones in good quality.

**Caparrapi Oil.** According to Mr. B. F. Tapia<sup>1)</sup> an oil obtained from a *Laurinea*, *Nectandra caparrapi* in a similar manner as oil of copaiba has been in use since quite a time in Columbia. The domestic name of the tree is "*canelo*", probably on account of the cinnamon-like odor of its bark. The oil is used in place of balsam of copaiba.

The color of the commercial oil is more or less dark in consequence of the heat applied for the removal of water admixed to the oil; otherwise the oil would be almost colorless. It contains a monobasic acid,  $\text{C}_{15}\text{H}_{26}\text{O}_3$ , which can only be obtained from the light-colored oil in crystals, melting at  $84.5^{\circ}\text{C}$ . The oil devoid of this acid consists largely of a sesquiterpene alcohol,  $\text{C}_{15}\text{H}_{26}\text{O}$ , called caparrapiol. By dehydrating agents this is readily converted into a hydrocarbon caparrapene  $\text{C}_{15}\text{H}_{24}$ . Both this and the alcohol are easily polymerized, particularly under the action of heat, so that about two-thirds of the oil used remain behind in a resinoid condition when distilled with water.

**Caraway Oil.** The present caraway crop in Holland has been quantitatively a good one, but the fruit proves deficient in essential oil, as is generally the case in damp summers. The distillation, therefore, is a less profitable one than last year, notwithstanding the cheap price of caraway and the rates for the oil will have to be raised soon.

<sup>1)</sup> Bull. soc. chim. Paris (3) 19, 638.

The yield of the crop in the various Dutch provinces amounted to:

in Groningen . . . .	about 5,000 bales
„ Northern Holland . .	„ 10,000 „
„ Sealand . . . . .	„ 14,000 „
„ Friesland . . . . .	„ 3,000 „
„ Southern Holland . .	„ 10,000 „
„ North Brabant . . .	„ 14,000 „
„ Other parts of the country	„ 4,000 „
<hr/>	
Total about	60,000 bales
old stock in addition	„ 15,000 „
<hr/>	

Total stock at the beginning of the present crop  
about 75,000 bales.

In consequence of weak demand the prices have remained low, but more recently some speculation has set in.

The crop in Sweden and Norway has been a normal one, furnishing considerable shipments of good quality to the market.

The reports from Eastern Prussia and from Russia are not yet complete.

The recently issued British pharmacopœia of 1898 states the specific gravity of oil of caraway as being 0.910 to 0.920. The fact is that the specific gravity of normal oil of caraway ranges between 0.905 and 0.915, generally somewhat below 0.910. Since normal oil of above 0.910 cannot always be had, it may be necessary for obtaining oil of the prescribed specific gravity, to remove from lighter oils some of the limonene. It would perhaps have been better to prescribe the removal of the total amount of limonene and, like the German pharmacopœia, give the preference to pure carvol.

**Cassia Oil.** The market of this oil had become rather dull during the Spring months but was considerably stirred in July by revolts taking place in the Chinese provinces of Kwangsi and Kwangtung. The reaction upon the price would have been much more marked if the insurrection had not occurred in the course of the hot season when there is little inclination and chance for speculation. In consequence the rise of prices has as yet been limited, not surpassing 5 to 6 d. per pound. They may remain stationary until the disturbances will have been suppressed, since all cassia oil in the markets of the world, is obtained from these two provinces.

Messrs. Carlowitz & Co. in Canton have favored us with the following report on the insurrection and its reaction upon the production of cassia bark:—

“The revolt in Kwangsi appears to be much more serious than first supposed. The rebels have occupied on their march from Yunghsien, 40 miles

south of Taiwo, the main centre of the cassia oil production, a number of places, among them Peiluhsien, Luchuenhsien and Sining and it is said that even Wuchow is in danger of being taken. They destroyed by fire several thousand piculs of cassia bark and several hundred piculs of cassia oil at Yunghsien. Although considerable quantities of both, bark and oil, had been received from Taiwo and Lotingchow, the market in these commodities was much disturbed and more than 10,000 piculs of cassia bark were disposed of. — In case this revolt is the outcome of a well laid plan aiming at higher results than the ransacking of a few cities, the French may choose to take welcome advantage of the situation by forcible intervention and surprise the English by some unexpected stroke. There are indications that the French have long since cherished the idea that the three southern provinces of China fall within the sphere of French interests and patronage.

According to recent advices the cities of Peilin and Luchuan are said to be besieged by the rebels and the cities of Heng-Yi and Pak-lau already to be in their hands.

Of course the cassia industry is greatly affected by these continued disturbances and shipments from the interior to Canton are subject to danger and to temporary stoppage."

**Cassia Oil "Schimmel & Co.", Pure Cinnamic Aldehyde,** absolutely free from chlorine. This excellent product has met with most favorable acceptance and due appreciation. In consideration of the constantly increasing number of readers of our Reports, we feel constrained to repeat some of the statements contained in our last Report (p. 13 to 14):—

Pure cinnamic aldehyde, free from chlorine, deserves the preference over any natural cassia oil; but also its price ensures to it the rank as a first rate article of trade. A comparison proves that it is cheaper than any of the best commercial cassia oils.

Our product is equally well adapted for all applications in perfumery and confectionary, in liquors, preserves etc. It affords us much satisfaction to have succeeded in supplying this synthetical oil at a price not higher than that of common cassia oil.

We beg to call special attention to the light color of our product, which constitutes a great advantage for its use in flavoring light colored soaps.

The oil is packed into aluminium cans similar in shape to the Chinese cans, each holding  $7\frac{1}{2}$  kilos net, 4 of these cans making one original case of 30 kilos ( $66\frac{2}{3}$  lbs.) net.

Aluminium cans offer the following advantages:—

1. Lightness. The weight of a Chinese cassia oil can is about  $2\frac{1}{2}$  kilos, whereas our aluminium cans weigh only 550 grammes, thus saving about 8 kilos of tare on each case.
2. Security. Our aluminium cans are exceedingly strong and hard. Their lower part, including the bottom, is made of one piece, they are nowhere soldered and resist handling much better than any other kind of packing.
3. Cleanliness. Aluminium does not act on essential oils, nor even on their color, as has been proved by protracted experiments,

whereas it is a well-known fact that natural cassia oil, kept long in the original tins, dissolves lead enough to render its use in food rather objectionable.

4. Neatness. It may be judged from the design on the special circular that there is no other packing approaching the solidity and finish of our aluminium cans, which both dealers and consumers, will appreciate for remaining permanently useful.

Soon after the introduction of aluminium cans, their regular supply offered some unexpected difficulties because the manufacture of seamless cans requires great skill and special appliances.

By experience and practice, however, these technical difficulties have been overcome and the continuous supply of aluminium cans is now secured.

**Cedar-wood Oil.** This much used oil continues to be appreciated as a valuable perfume of soaps. The extensive German lead-pencil establishments enable us to manufacture the oil on a very large scale and successfully to meet the competition with America and France.

**Chamomile Oil.** In consequence of the rainy and damp weather during the months of April, May and June, the crop has been a short one in Germany and Hungary. As a result the price has risen by nearly 100 per cent and that of the oil will soon follow.

**Cinnamon Oil, Ceylon.** The prices of fine cinnamon-bark and chips have been continually rising and justify higher rates for genuine distillates.

Notwithstanding the export of cinnamon bark and chips has considerably increased, amounting to:—

1,413,371 kilos of bark during the period of Jan. 1<sup>st</sup> to Aug. 30<sup>th</sup> 1898  
 743,208 „ „ chips „ „ „ „ „ 1<sup>st</sup> „ „ 30<sup>th</sup> 1898  
 During the same periods in 1897 it amounted to 1,399,855 kilos of bark and 704,004 kilos of chips.

**Cinnamon-leaf Oil.** We received a large shipment of this oil direct from Ceylon by one of the last steamers and have stored part of it in our Hamburg warehouses. Orders for delivery at Hamburg may now be solicited. Original cases containing 36 vials each at 22 oz. are charged at 22 kilos net.

**Citronella Oil.** We have recently exerted ourselves to obtain further and more accurate information about the commercial and scientific relations of this important commodity. Our Mr. Karl Fritzsche, generously assisted by Messrs. Volkart Brothers in Galle, has recently studied the production of citronella oil on Ceylon. He has sent us the following report:—

“Citronella grass is cultivated exclusively in the Southern Province of Ceylon, mainly between the rivers Ginganga in the north-west and Wallaweganga in the east. The grass grows only on the declivities of hills, unless

they are occupied by brush-wood or by tea-plantations, which have recently been cultivated with much success. The grass reaches a height of about 1 meter and stands irregularly scattered in tufts. Ferguson states in his rather antiquated "Handbook of Ceylon", dating from the years 1896 to 1897, that 30,000 to 35,000 acres of land were occupied by citronella plantations. But since the compilation of that book the cultivation of citronella grass has rapidly increased and competent dealers estimate the present extent of the plantations at 40,000 to 50,000 acres of land. Exact figures will hardly be obtainable before the government will institute an official census.

The plants seem to require little, if any, care; but the harvests must be gathered regularly in time, because otherwise the spikes would grow too luxuriantly and partly decay. Although the climatic condition on Ceylon admit a constant growth of the vegetable world irrespective of seasons, so that harvests could be gathered throughout the year, the crops of citronella are generally cut but twice a year, one in July or August, and one in December, January or even February. The first and most productive one preceeds the north-east monsoons at a time when the hands necessary for cutting, harvesting and distillation can most conveniently be had. In September and October, before the rainy season sets in, the laborers are needed in the rice fields. The second harvest begins before the time when the rice fields have to be made ready for the south-west monsoon which occurs during April and May. The gathering of the citronella grass, therefore, takes generally place at a time when the coolies are not engaged in the care of the more important rice fields. It sometimes even happens that citronella plantations are left uncut for one or two harvests for want of laborers. The yield of oil is estimated at 16 to 20 vials, each containing 22 oz., per acre for the summer crop, and 5 to 10 vials for the winter crop. Exact figures can hardly be given since the produce varies according to the age of the grass, the weather and the local conditions of the various plantations. The longer an estate is worked, the less oil it is said to yield even under favorable conditions of weather and soil. After the lapse of 15 years the vitality of the grass seems to be exhausted and the raising of new plants becomes necessary in order to keep the estate in a remunerative condition.

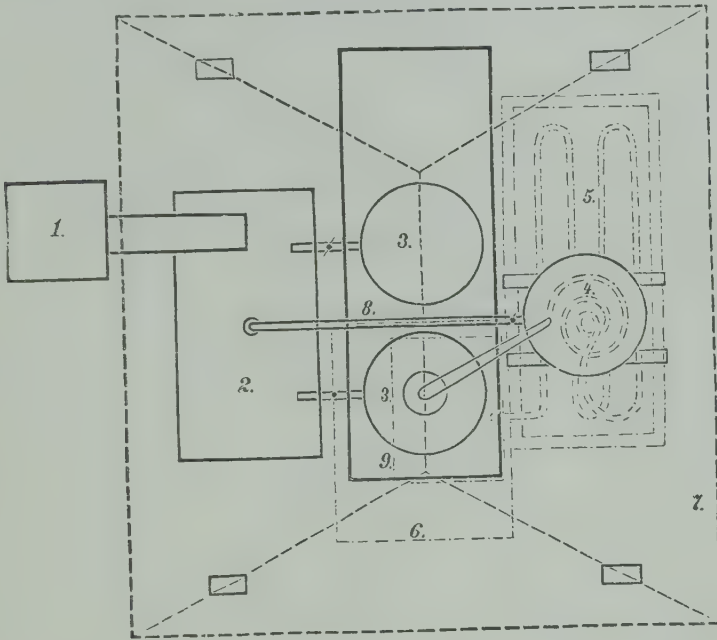
In addition to a rather neglected plantation in the neighborhood of Galle, I visited the country between Matara and Akuressa, located in the centre of the citronella districts, and also the tract between Akuressa and Henegama. The distilleries are located at the base of the ridges and hillsides where cool water is to be had in sufficient quantity. They are readily observed in the barren tropical landscape by their low and clumsy chimneys, about 13 feet high. In most cases the construction of these distilleries is by no means the alleged primitive one and it is surprising how well the natives, who constitute the greatest part of the producers, have succeeded in the construction of their distilleries. These are generally located under a protecting shed, and consist of a steam-boiler with a safety-valve and water-indicator resting upon a solid foundation, of two cylindrical iron stills, mostly 6 to 7 feet high and 3 to 4 feet in diameter. They are furnished with a common interchangeable alembic and are connected with a large wooden barrel containing the serpentine cooler and underneath a large subterranean receptacle for the collection of the distillate. This is located in a basin which can be locked in order to prevent pilfering of oil.

The following diagrams will sufficiently explain such a distillery.

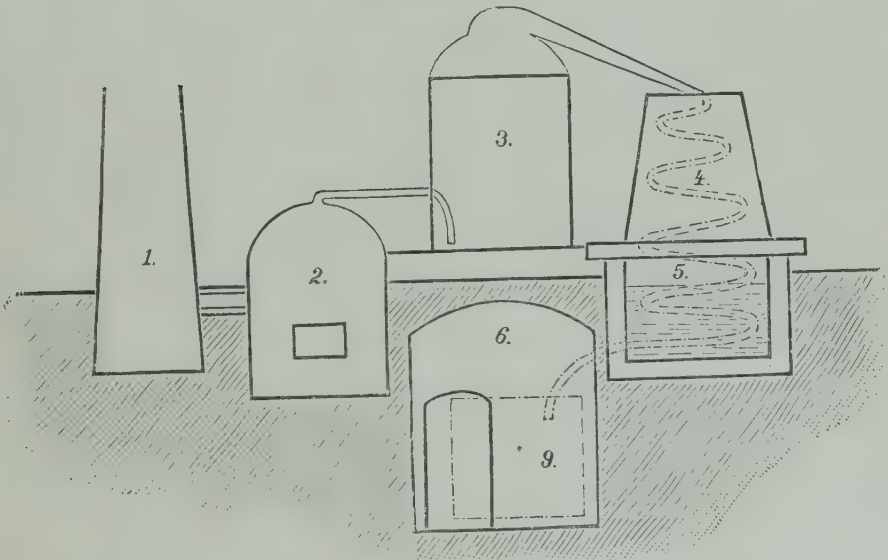
The distillation consists in direct steam-distillation without the addition of water to the grass. The warm water passing from the cooler is used for feeding the boiler while the lower basin (5) through which the serpentine tube passes serves for a final cooling of the distillate. The only thing abnormal is that the distillate is collected and preserved without a prompt separation of the oil and the water. The reason is said to consist in the fact that the coolies are prone to stealing and cannot be entrusted with the collection of the pure

oil. When a certain amount of distillate has accumulated in the large basin in the cellar, which is kept under lock, the proprietor bottles the oil, while the aromatic water is allowed to run away.

Top view.



Side view.



1. Chimney. 2. Steam-boiler. 3. Still. 4. Cooler. 5. Cooling basin. 6. Cellar for collecting the distillate. 7. Shed. 8. Steam-pipe. 9. Basin for collecting and preserving the distillate.

Each distillation requires about 6 hours or longer, as labor and material do not count much. For the management of such a distillery there are necessary:—

- 10 women for cutting and binding the grass into bundles,
- 3 coolies for loading and bringing it to the distillery,
- 3 coolies for attending to the boiler and still.

The wages for coolies are 37½ cents per day, for women 18 cents per day. Fuel does not cost anything as the exhausted grass from the stills, after having been dried in the sun, serves as fuel. The Southern Province of Ceylon is devoid of wood so that the working of the distilleries has to be stopped for want of fuel as soon as the rainy season sets in and the refuse grass cannot any more be dried in the sun. The total expenses for running a plant, therefore, consist only of the wages for laborers and the wear and tear of the distilling apparatus, which, however, is inconsiderable.

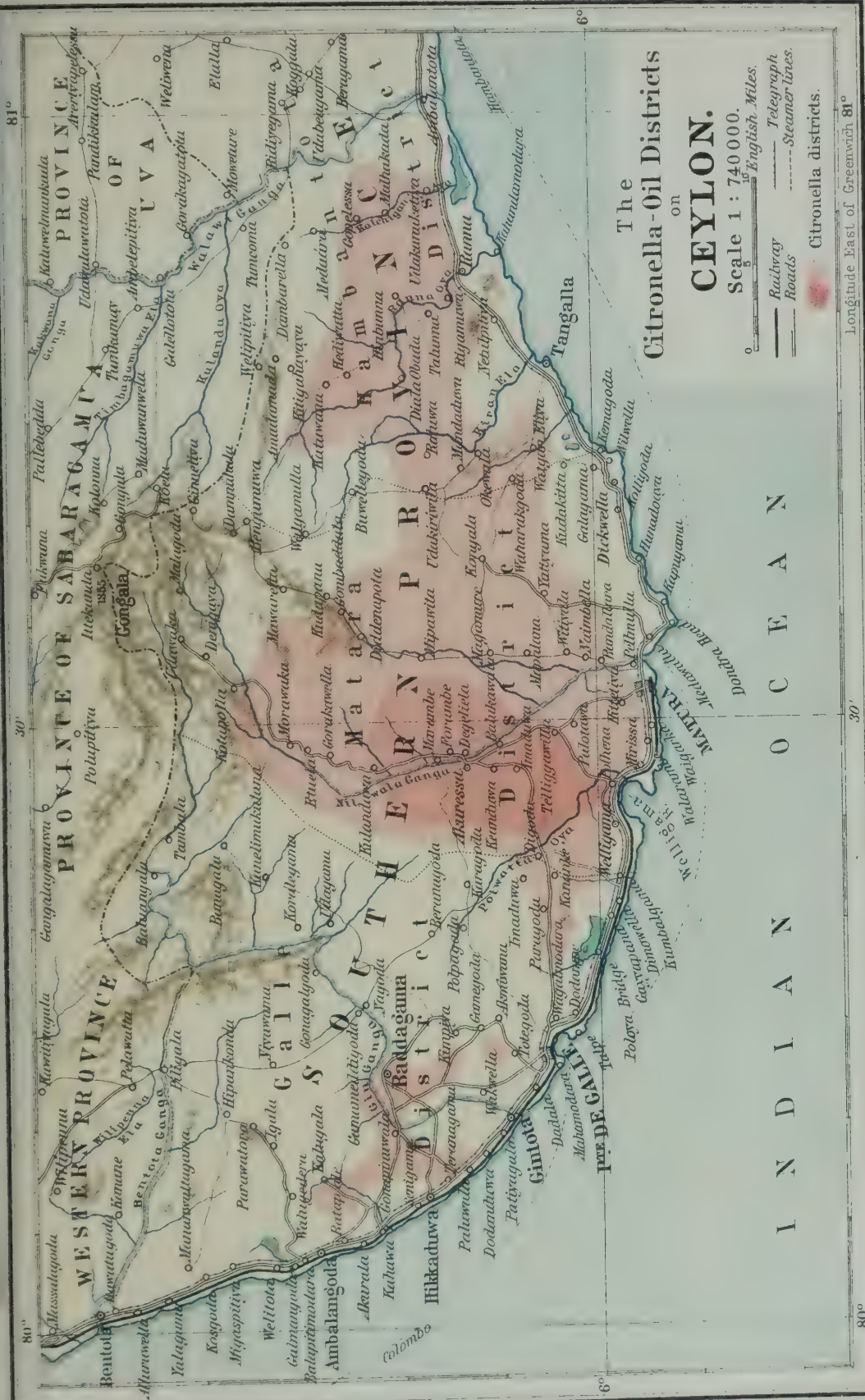
A still of 7 feet in height and 4½ feet in diameter produces about 16 to 20 vials, each holding 22 oz. of oil per day, equal to 360 to 440 oz. The weight of the grass put into the still is never ascertained, the still is simply filled with the dry grass and the steam turned on. A special drying of the grass is not customary. When the grass is cut, it always takes several hours before it reaches the still and this time, at the tropical heat, is sufficient to deprive the grass of most of its moisture. Exact figures about the percentage of yield of the grass therefore are wanting. This varies considerably at the various seasons; the yield is smaller at the second cut in January and February, when the grass blooms, while it is much larger in July and August after the monsoon rains, when about 18 vials = 406 oz. of oil are expected from each acre of land against 125 to 150 oz. in January.

In some localities common stills with fireplace underneath are said to be still in use. In this case, of course, the grass is distilled with water. Most citronella oil, however, is now obtained by steam distillation."

The annexed map shows the principal districts of citronella grass cultivation upon Ceylon. The total number of stills is estimated at 600, producing about 1,000,000 lbs. of oil per annum. Ferguson enumerates in his book on Ceylon, cited above, the following principal districts of citronella grass cultivations:—

Estate	Citronella	near Akuressa	about	1400 acres
"	Wilpita	"	"	800 "
"	Charley Mount	"	Weligama	" 900 "
"	Rose Neath	"	"	" 500 "
"	"Fred's Ruhe"	"	Hikkaduwa	" 250 "
"	Wallahandova	"	Galle	" 390 "
"	Ratmaherre	"	Dodanduwa	" 260 "
"	Katherine Valley	"	Kataluwa	" 280 "
"	Karayaldeniya	"	Akuressa	" 180 "
"	Nidenwela	"	Weligama	" 150 "
"	Danapatiya	"	"	" 220 "
"	Galduwewadda	"	Weragoda	" 200 "
"	Miriswatta	"	Tangalla	" 200 "
"	Rose Wood	"	Galle	" 100 "
"	Mellagalpathe	"	Weligama	" 100 "
"	Karayalemyawatte	"	Kataluwa	" 125 "
"	Panapittygalla	"	Balapitiya	" 154 "
"	Udabatalahena	"	Parawahera	" 100 "
"	Borakanda	"	Ambalagoda	" 100 "
"	Kananka	"	Akuressa	" 150 "

The largest export figure is recorded for the year 1897, amounting to 1,182,867 lbs.; this will still be considerably exceeded by the



The  
Citronella-Oil Districts  
on  
**CEYLON.**  
Scale 1 : 740 000.  
English Miles.  
— Railway  
— Roads  
— Telegraph  
— Steamer lines.  
Citronella districts.

81° 30' 80° 30' 80°  
Longitude East of Greenwich 81°



figures of the present year, since the shipments of citronella oil up to August 30<sup>th</sup> (the first 8 months) amounted already to 1,021,626 lbs. against 781,832 lbs. during the same term in 1897.

Of this quantity there were exported to:—

England . . . . .	461,692 lbs.
America . . . . .	521,601 „
Germany . . . . .	17,425 „
India . . . . .	9,920 „
Australia . . . . .	4,792 „
France . . . . .	3,440 „
China . . . . .	2,012 „
Singapore . . . . .	504 „
Africa . . . . .	240 „

Total: 1,021,626 lbs.

When compared with the plantations on Ceylon, those of the Straits Settlements near Singapore are almost insignificant. In the "Singapore and Straits Directory for 1898" we notice the following citronella producing estates:—

Estate Ceylon Epoh., Province of Negri Sembilan	500 acres
„ Hardouin, „ „ Wellesly	40 „
„ Perseverance, „ „ Singapore	450 „

The "Selangor Plantations Syndicate", Limited, recently organized in the Straits Settlements, has entered upon the production of citronella oil. According to a sample recently received, this oil is of exceedingly fine quality, containing as much as about 90 per cent of geraniol and being readily soluble in 1½ volumen or more of 80 percent alcohol.

Efforts are also being made on Java to secure trade in citronella oil and we may soon have occasion to refer more explicitly to this source of supply.

We are in receipt of twelve specimens of citronella oil obtained by our Mr. Karl Fritzsche from well known producers on Ceylon. Upon examination of these oils we obtained the following results.

The specimen No. 14 was an oil picked out from our stock in order to place it into comparison with the recently obtained specimens. No. 8 represents an oil recently obtained from the Straits Settlements. None of these 14 oils showed any indication of sophistication.

The essential constituents of citronella oil, as is known, are the alcohol geraniol and the aldehyde citronellal. The well known acetylizing method<sup>1</sup>) applied by us for a series of essential

<sup>1</sup>, A description of the acetylation process will be found in our Report of October 1894, page 62, and tables for calculation in our Report of October 1897, pages 76 to 83.

oils for the quantitative estimation of their alcoholic constituents, serves in this case not only for the determination of geraniol but equally well for that of citronellal, inasmuch as this is completely<sup>1)</sup> converted into isopulegol acetate<sup>2)</sup>, isomeric with geranyl acetate,

No.	Marked	$\alpha_D$ at 20°	Spec. grav. at 15°	Amount of geraniol <sup>3)</sup> per cent	Solubility in 80 percent alcohol
1.	J. F. 1.	— 0° 46'	0.892	88.6	{ 1:1 to 7 clear; 7 to 10 opalescent turbidity.
2.	J. F. 2.	— 0° 54'	0.892	80.9	id.
3.	J. F. 3.	— 0° 48'	0.892	82.5	id.
4.	W. 1.	— 1° 18'	0.890	85.4	{ 1:1 to 4.5 clear; 4.5 to 10 turbidity.
5.	W. 2.	— 1° 32'	0.886	85.1	id.
6.	W. 3.	— 2° 20'	0.888	83.4	id.
7.	W. 4.	— 1° 25'	0.894	81.8	{ 1:1 to 8 clear; 8 to 10 opalescent turbidity.
8.	St. S.	— 0° 53'	0.890	90.6	1:1 to 10 clear.
9.	VII.	— 7° 10'	0.919	56.9	{ 1:1 to 4 clear; 4 to 10 milky turbidity.
10.	VIII.	— 0° 34'	0.888	86.4	{ 1:1 to 4 clear; 4 to 10 opalescent turbidity.
11.	S. V.	— 9° 53'	0.915	65.5	{ 1:1 to 10 clear; slight turbidity after one hour.
12.	W. VI.	— 20° 37'	0.896	50.4	{ 1:1 to 3 clear; 3 to 7 great turbidity; 7 to 10 slight turbidity.
13.	L. B.	— 7° 13'	0.918	54.1	{ 1:1 to 3 clear; 3 to 10 great turbidity.
14.	Sch.&Co.	— 9° 36'	0.908	61.1	{ 1:1 to 4 clear; 4 to 10 slight turbidity.

when acted upon by acetic acid anhydride. The total amount of these two substances may well serve as an indicator of the quality of citronella oil. The figures obtained by this method of estimation are nearly coincident:—

1.	Acetylation of sample 1.	Figure of saponification = 259.7 = 88.6 per cent
2.	" " " 1.	" " " = 258.6 = 88.1 " "
1.	" " " 14.	" " " = 190.8 = 61.1 " "
2.	" " " 14.	" " " = 190.0 = 60.9 " "

Mr. J. C. Umney<sup>1)</sup> has also recommended the acetylizing method for the estimation of oil of citronella, claiming a minimum amount of 60 per cent of geraniol. For want of sufficient authentic material we can as yet not advance a definite norm, deem, however, 60 per cent as being too low a standard.

<sup>1)</sup> See our Report, October 1896, p. 44.

<sup>2)</sup> Tiemann and Schmidt, Ber. d. deutsch. chem. Ges., Vol. 29, p. 913.

<sup>3)</sup> The amount of geraniol includes here also that of citronellal, as will be explained subsequently.

<sup>4)</sup> Chemist and Druggist, Vol. 48 (1896) p. 356.

In order to recognize an admixture of kerosene or fatty oil to citronella oil, we proposed in our Bericht of October 1889 (p. 22) the solubility with 80 percent alcohol by volume (sp. gr. of 0.8631 at 15.5°) as a fair criterion of quality. One part of the oil must render a clear or but slightly opalescent mixture with 2 to 3, as also with 10 parts by volume of 80 percent alcohol at +20° C., nor should there take place any separation upon standing.

Our attention was called to an apparent discrepancy in the results of this test it being stated that with some oils it would fail to indicate an admixture of 5 and even 10 per cent of kerosene. At the same time two oils were submitted to us of which one was said to allow 5 and the other one even 10 per cent of kerosene admixture without being dedected by our test. The results of our examination are recorded in the table above. No. 12 was said to admit a admixture of 5 per cent of kerosene by "absorption". Although some error evidently exists here, we have not failed to prepare such mixtures in exact proportions with 5 and 10 per cent of kerosene (sp. gr. 0.799 at 15° C.) Our method of testing, as was to be expected, was, however, in every case sufficient for establishing beyond doubt the presence of the admixture, as the following figures prove:—

No.	Amount of petroleum	$\alpha_D$ at 20°	Sp. gr. at 15°	Solubility in 80 percent alcohol
II.	5 per cent	—9° 10'	0.911	{ 1:1 to 4 clear; at 4 to 10 great turbidity.
II.	10 " "	—8° 53'	0.903	{ 1:1 to 2½ clear; at 2½ to 10 great turbidity; drops on top.
12.	5 " "	—19° 43'	0.894	{ insoluble in 1 to 10 volumes; drops on top.

The above enumerated 14 oils, according to the result of their examination, may be divided into two groups, one with a high percentage of geraniol, with a low optical rotation and low specific gravity (Nos. 1 to 8 and No. 10), and another group with a lower percentage of geraniol, a higher optical rotation and specific gravity (Nos. 9, 11, 12, 13 and 14). Messrs. J. C. Umney and R. S. Swinton<sup>1)</sup> have already pointed out this difference, supposing the higher specific gravity and the lower percentage of geraniol, to be due to the presence of a sesquiterpene. They believe that the substance isolated by them from the parts having the highest boiling point (245° to 280°), is a sesquiterpene, which however shows no identity with any one of the known sesquiterpenes. We also have fractionated such an oil having the sp. gr. of 0.915 (No. 5 of the above table) after it had been saponified. We obtained, besides much of camphene with a strong optical rotation,  $\alpha_D = -55^\circ 0'$ , beyond the boiling point of geraniol, a fraction having a strong odor of

<sup>1)</sup> London Pharmac. Journ. Vol. 59 (1897) p. 138.

methyl-eugenol. This yielded, upon oxidation by means of potassium permanganate, veratric acid melting at 179°, being the characteristic product of oxidation of methyl-eugenol. There are two different species of citronella grass distilled upon Ceylon, but it is unknown whether they were varieties or a degeneration of *Andropogon Nardus* L. In any case, the products represent one oil richer in geraniol and of lighter specific gravity and another, heavier, but poorer in geraniol.

We shall continue our researches of oils of various derivation with a view to settling any doubts still prevailing.

**Clove Oil.** The harvest of cloves beginning in the course of the present month is said to be an inferior one on Zanzibar and Pemba in consequence of persistent drought and therefore may not even equal the very short crops of last year. Speculation has already begun with better chances than those of the last one by a London clique.

Meanwhile interesting reports about cloves and some other products of Zanzibar have been published by Mr. R. N. Lyne, Agricultural Director of Zanzibar. An endeavor has been made to improve the quality of African cloves so as to attain to the same good quality as the preferred Penang and Amboyna sorts possess. These efforts have been fairly successful except that the machinery employed has proved to be deficient. The main object is the separation and elimination of the stalks from the fruits, of which the Zanzibar cloves still contain an undue admixture, while the Penang and Amboyna cloves are free from any stalks and therefore yield 1 to 2 per cent more oil.

Another improvement consists in a better method of drying, which appears to be done to an excess by the Arabs. They expose the cloves to the tropical heat of the sun until they acquire an almost black color, losing thereby a considerable amount of essential oil. It has been proposed to effect the drying under glass-covers. Since the abolition of slavery the Arabs are short of help so that part of the clove crop of 1897 had to remain unplucked on the trees.

The yield of crops of the last three years is stated to have been:

in 1895.	On Zanzibar	146,391 frasilas	
	„ Pemba	391,451	„
	Total	537,845 frasilas each 35 lbs. =	18,814,575 lbs.
„ 1896.	„ Zanzibar	119,784 frasilas	
	„ Pemba	242,085	„
	Total	361,869 frasilas each 35 lbs. =	12,665,415 lbs.
„ 1897.	„ Zanzibar	91,571 frasilas	
	„ Pemba	240,950	„
	Total	332,521 frasilas each 35 lbs. =	11,638,235 lbs.
Average yield per annum 410,745 frasilas each 35 lbs. = 14,376,075 lbs.			

One half of this annual production is shipped to Bombay, the other half in about equal parts to London, New York and Hamburg.

The prices of Zanzibar cloves, ranging from *M.* 40.— to 42.— at the beginning of the present year, reached *M.* 78.— at the end of March. In the course of the last six months they have gradually advanced to *M.* 80.— to 84.— per 100 kilos loco Hamburg, duty not included. The present quotations for oil of clove correspond to these rates.

Clove stems have become constantly scarcer. The only explanation of this fact seems to consist in a want of labor for the proper elimination of the stalks from the fruits.

The import of clove stems in the principal market, Hamburg, was in

1895 . . . . .	about 350,000 kilos
1896 . . . . .	„ 454,000 „
1897 . . . . .	„ 150,000 „

showing a decrease of one third within the last year. Oil of clove stems, therefore, has considerably risen in value. It appears to us that the want of stems also has exercised some influence upon the market value of cloves.

**Cognac Oil.** The producers have raised their prices in consequence of the failure of the present crop of grapes. Want of proper wine yeast will soon be felt.

We have received from Spain a distillate nearly of the same good quality as the Rhenish product.

**Coriander Oil.** The crop in Thuringia has yielded a normal result so that sufficient material is in the domestic market to render it independent of any outside import. Moravia and Russia have also had good harvests.

**Cypress Oil.** The demand for this oil so efficacious in hooping-cough (*pertussis*), has been an unusual one during the last months. The excellent and prompt action of the oil is more and more recognized. Its application gives relief within 1 to 2 days and subsequently a normal and prompt restauration of the affected membranes.

The application consists in spreading a few drops of the oil upon the pillow of the patient, as also by aromatisation of the sick-chamber with the oil by means of an atomizer.

**Dill Oil.** Mr. John C. Umney has recently published a paper<sup>1)</sup> about the commercial sorts of dill-fruit and the essential oils obtained therefrom. He states that no perceptible difference exists between German and English fruits. Flückiger and Hanbury<sup>2)</sup> have already pointed out that a discrimination between European and Indian dill

<sup>1)</sup> London Pharmac. Journ. Vol. 61 (1898), p. 176.

<sup>2)</sup> Pharmacographia p. 328.

and the separation of the latter under the species name of *Anethum Sowa* on account of slight botanical variations is uncalled for. Umney, however, does not share this view and makes a distinction between European and Indian dill on account of the difference between their essential oils.

We were the first to call attention in our Report of October 1891, p. 21, to a constituent of Indian dill oil heavier than water and not present in ordinary dill oil<sup>1)</sup>. Meanwhile Messrs. Ciamician and Silber have shown this substance to be an isomer of petroselinum-apiol. As Japanese dill oil in all its properties is identical with Indian oil and as the Japanese fruit shows the same botanical characteristics as the fruits of Indian dill, both seem to be of the same botanical origin.

The physical properties of the dill oils mentioned by Mr. Umney are:

	sp. gr.	opt. rot.
1. English oil (Market Deeping)	0.9148	+72.25°.
2. " " (Canterbury)	0.9146	+80.25°.
3. German " . . . . .	0.9002	+70.25°.
4. Indian " . . . . .	0.9486	+47.5°.
5. Japanese, " . . . . .	0.9643	+50.5°.

Mr. Umney here says verbally:

"The oil distilled from the German fruits has practically the same characters as that distilled from the English fruits provided that no separation of carvol has taken place, as in sample No. 3, a practice adopted to some extent on the continent."

We cannot but earnestly request Mr. Umney henceforth to omit such wanton insinuations, alledged with a view to discrediting German competition, evidently inconvenient to Mr. Umney.

The sp. gr. 0.0002 is a low one even for German dill oil, but the following table of physical constants obtained with oils of our own distillation will show that such a low specific gravity is nothing uncommon.

	Sp. gr.	angle of opt. rot.
1. Thuringian dill . . . . .	0.911	—
2. " " . . . . .	0.907	—
3. " " . . . . .	0.906	—
4. " " . . . . .	0.909	—
5. " " . . . . .	0.910	+76°
6. " " . . . . .	0.902	+78° 32'
7. " " . . . . .	0.899	+79° 13'
8. " " . . . . .	0.908	+76° 17'
9. Russian " . . . . .	0.909	—
10. English " . . . . .	0.906	+80° 2'
11. Spanish " . . . . .	0.913	+50° 21'
12. Indian " . . . . .	0.970	+41° 30'

<sup>1)</sup> Our Report, April 1897, p. 15.

From this table it is evident that pure dill oil may have even a still lower specific gravity than 0.900, as also that oil distilled from English dill not always has the high specific gravity mentioned by Mr. Umney.

When the new British pharmacopœia assumes that the percentage of carvol is an indicator of the value of oil of dill and accordingly requires a sp. gr. of 0.905 to 0.920, no objection can be advanced against this notion. It could, however, be an error, without other evidence, to consider an oil as sophisticated which does not come up to this requirement.

The English oil No. 10 and the Spanish one No. 11 are so rich in phellandrene as at once to show the reaction of phellandrene when acted upon by sodium nitrite and acetic acid. With German oils this reaction could only be obtained by application of the lower fractionates from a greater quantity of oil.

Whether the oils of dill and of caraway differ only in the presence of phellandrene may at present remain undisputed.

### Essential Oils, Sicilian and Calabrian.

The crop of Italian agrumen fruits of the season 1897/98 is estimated at 2880 million fruits. It therefore amounts to about 400 millions less than the officially calculated average yield of the last ten years.

Of the four districts from which agrumen fruits are exported, namely South-eastern Italy, South-western Italy, Sicily and Liguria, only South-western Italy and Liguria had a normal crop, amounting to 780 million fruits for the first and 40.7 million fruits for the last named district; South-eastern Italy reached only half of its normal crop, namely 44.6 millions of fruit and Sicily 1980 millions against 2540 millions last year. The shortage, however, extended less to lemons than to oranges; it also became soon noticeable by the rates. The extraordinary price of 51 lires was paid in March 1898 for 1000 best Palermo oranges packed in 5 boxes, in April the price declined to 38 lires. For 1080 lemons 9 to 15 lires were paid according to quality. Rejected lemons good enough for the manufacture of citric acid brought 3.50 lires per 120 kilos.

Little can be reported about the condition of the market during the last six months. The comparatively small stock of all kinds of agrumen oils caused considerable price fluctuations, with a rising tendency. The quotations would have reached far higher figures but for the fact that the exports thus far have been inconsiderable.

The following statistical figures demonstrate the fact that the exports during the first eight months of the present year are less by one quarter than they were during the same term last year:—

The exports from Messina during the months of January to August were in 1897

544,567 kilos against  
391,038 „ during the same term in 1898,

this makes 153,529 kilos less in 1898.

The demand for agrumen oils from America has been one third less this year, it receiving the following imports:—

in 1897 from January to August 189,319 kilos  
„ 1898 „ „ „ „ 120,052 „

The principal cause for this decrease may have been the unusually large imports of Sicilian and Calabrese oils into the United States in 1897, amounting to 247,104 kilos, while they amounted

in 1896 . . . . . to 160,845 kilos  
„ 1895 . . . . . „ 177,706 „  
„ 1894 . . . . . „ 227,027 „  
„ 1893 . . . . . „ 192,217 „

A retardation of business caused by the recent war may also have contributed to this reaction.

The efforts recently inaugurated to allay the agrumen or rather the lemon crisis, tending to a more remunerative use of the fruits, may also be referred to. It is designed to combine most of the producers, jobbers and manufacturers in a stock-company "*Consorzio agrumario*" and thereby to organize united action with common interests. The principal object and aim of this stock-company shall be to purchase by their agents all the lemons unfit for export in cases, and to work them first for oil and subsequently for citric acid.

The originators of this scheme hope to form a monopoly in order to henceforth control the prices of lemon oil and citric acid at home and abroad. In this way it is hoped to secure for producers fairer returns for all rejected fruits commensurate with the cost of production.

The success of this scheme may not be without some chances of success, but the obstacles against its realization seem to be more considerable than had been expected and may ultimately frustrate the whole venture.

**Bergamot Oil.** Oil of superior quality was scarce and had a buoyant tendency during this season, reaching as much as *M.* 18.50 to *M.* 21.— per kilo. The prices have somewhat declined in September but the stock is said to be a small one, so that a return to higher rates may be expected.

The outlook for the new crop is not favorable, hardly more than half as many fruits than last year's crop being expected. Granted that the fruit may be richer in oil this year than last one, the result

cannot be better by more than 20 or 25 per cent. However that may be, this year's production of oil of bergamot will be small in comparison with that of last year, itself a deficient one. Stocks also seem to be small both in Calabria and in other countries, and a higher average price must be expected this season than at the preceeding one. Moreover, the oil of this season will likely be wanting in its normal amount of ester so that oils of standard quality will be scarce and command high prices.

Messrs. Soldaini and Bertè in continuation of their former researches, have studied the methods of the discovery of adulterants in oil of bergamot<sup>1</sup>). By fractional distillation they prepared a series of fractions each of equal volume of pure oil of bergamot and ascertained the optical rotation of each fraction. On the other hand, they applied the same experiment to oils mixed with 2.5 to 5 per cent of turpentin oil or lemon oil and compared the figures obtained. The investigators propose, however, to repeat the experiment next season in order to ascertain the reliability of the results.

**Lemon Oil.** After constant fluctuations the prices of this important commodity have reached *ℳ* 8.— per kilo, but have recently declined to *ℳ* 7.—. The present harvest was at first considered a deficient one in quantity, it appears, however, according to more recent estimates to equal the average yield of last year. In no case it will reach a normal amount. It is therefore likely that the prices will be somewhat higher this season, the more so as the stock of oil may nearly be exhausted before new supplies will arrive upon the markets. Furtheron, the combine referred to in the introductory lines of this report on essences, may exercise some influence upon the value of lemon oil inasmuch as its objects are preeminently aimed at a more remunerative utilization of the production of lemon fruits.

The following note, quoted from the "Deutsches Handels-Archiv" of 1898 may not be amiss:—

"The cultivation of agrumen fruits particularly of lemons on the peninsula of Sorrento has fairly succeeded, especially in the neighborhood of Sorrento and along the coast of Amalfi. 315,000 cases of lemons were shipped from Sorrento and 92,931 cases from Maiori, near Amalfi, in 1897. They went to England, North America and a small part to Hamburg."

The manufacture of lemon oil, however, as far as we are informed, is not yet carried on in the Sorrento district.

Messrs. Umney and Swinton<sup>2</sup>) allege to have found a new constituent in oil of lemon. In distilling in a vacuum 2 kilos of

<sup>1</sup>) *Sull' analisi dell' essenza di bergamotto. Estratto dal bollettino chimico farmaceutico* Milano 1898.

<sup>2</sup>) *London Pharmac. Journ.* Vol. 61 (1898), p. 196.

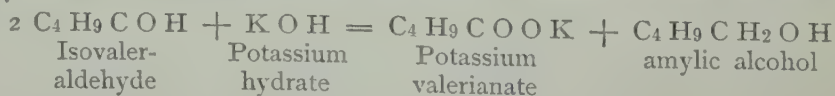
lemon oil, they obtained 300 Cc. of the fraction having the highest boiling point. In order to ascertain the amount of constituents that can be acetylated, the concentrated oil was boiled for two hours with acetic anhydride. The product of the reaction was shown to contain 68 per cent of saponifiable constituents. It is a well known fact that citronellal, but not citral, can be quantitatively determined by acetylation. Therefore no conclusion can be obtained thereby as to the quality of the original oil. They tried to determine the amount of aldehyde contained in the oil by means of the bisulfite-method in a cassia oil flask<sup>1)</sup>, without, however, attaining to any approximately correct result, since the bisulfite compound of citronellal is insoluble in water and remains suspended in both the aqueous and the oily stratum, thereby preventing any distinct sight and reading of the scale. Although neither acetylation nor the determination of the amount of aldehyde afford any evidence of the quantity of aldehydes and alcohols present, the authors conclude from their experiments the presence of esters. They decomposed (apparently in the oil not yet acetylated) the aldehydes present by boiling it with alcoholic potassa solution, and subsequently submitted the product to distillation, at first in a vacuum and then under ordinary pressure. They obtained between 230° to 250° a fraction of the characteristic odor of geraniol. They isolated this alcohol by repeated fractionation. Its properties were found to approximate those of geraniol, but they omitted to specify this apparent identity; nor have the authors prepared any of the characteristic derivatives of geraniol. It, therefore, remains unsettled whether the substance obtained by Messrs. Umney and Swinton really is geraniol.

Should the authors furnish supplementary evidence, the method of preparation described by them would still leave it doubtful whether the geraniol is a constituent of lemon oil, or whether it originated by the method of treatment in the process described. For the possibility that geraniol may be formed by the action of alcoholic potassa solution upon citral is by no means excluded<sup>2)</sup>.

Similar considerations apply to the presence of acetic acid alleged to be found in the saponification liquor. The authors have

1) In our Report, October 1895, p. 15, we have called the attention of Mr. Umney to the fact that his notion to call the cassia oil flask "Hirschsohn's flask" is incorrect. This flask has been devised and introduced by us. His continuous designation "Hirschsohn flask" therefore is not justified by any facts.

2) Alcoholic alkali acts not only upon aromatic aldehydes, but also upon those of the fatty acid series, giving rise to the formation of the corresponding alcohol and acid. Isovaleraldehyde for instance reacts according to the following equation:—



(Borodin, Jahresber. f. Chem. 1867, 337).

also failed to furnish any analytical proof and derivatives. Granted that acetic acid really was found, there remains substantial doubt as to its origin, inasmuch as the formation of acetic acid is well possible in the decomposition of aldehydes.

Although we deem it not excluded, it seems to us for the present doubtful whether geranyl acetate can be considered a constituent of oil of lemon. In any case it would be requisite to furnish substantial evidence for the alleged presence of geraniol and acetic acid in the reaction products described by Messrs. Umney and Swinton. It should furthermore be demonstrated, whether not or whether any of these two substances did really originate from aldehydes present by the processes employed by the authors.

**Mandarin Oil.** This oil was known to contain much limonene and little citral. Messrs. Flatau and Labbé<sup>1)</sup> recently have submitted the oil to a close examination and have found it to consist of 98 per cent of limonene, traces of citral and of 1 per cent of the same ester, insoluble in alcohol, as is contained in sweet orange oil.

**Orange Oil, bitter.** The price of the unsophisticated fine grades of this oil have been raised by several marks in the course of the present season. Its production is a very limited one. No essential change of prices is to be expected for the present.

**Orange Oil, sweet.** In consequence of considerable sales on delivery and the procuring of the requisite amounts of oil, its price rose to *M.* 18.50 per kilo.

The crop of oranges promised to be an abundant one during and after the flowering time, but persistent damp and cool fogs coming from the Mediterranean sea and drifting far into the lands have impaired many of the young fruits and caused their premature dropping. A fair average harvest of oranges and a decline of the price of the oil is nevertheless expected.

Since the considerable reduction of the freight rates from Southern to Northern Italy the trade in and use of, fresh oranges in Upper Italy has enormously increased. Large quantities of fruits, heretofore employed for obtaining essential oil, now find a more remunerative use and enable the producer to obtain better prices for rejected fruits. The rates of orange oil, therefore, will henceforth maintain a more steady level.

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Professor Wallach had already shown that the oil of sweet oranges consists mainly of limonene. Besides, it was known to contain some citral and a small quantity of an oxygenated compound. According to recent statements of Messrs. Flatau and Labbé<sup>2)</sup>

<sup>1)</sup> Bull. soc. chim. Paris (3) 19, 364.

<sup>2)</sup> Bull. soc. chim. Paris (3) 19, 361.

myristinic acid and myristicol(?) are said to exist in slight quantities in the oil. Since the characteristic odor of Portugal oil is not due to the terpene alone, these investigators have entered upon a closer enquiry into the constituents of the oil, particularly the oxygenated ones.

When agitating the oil with bisulfite solution they obtained a double compound, which yielded, besides traces of citronellal, a small amount of a new aldehyde with a very characteristic odor of oranges. Upon saponification a small quantity of alkali was absorbed, indicative of the presence of an acid or ester. A certain quantity of the oil was deprived of the fractions boiling below  $179^{\circ}$  under ordinary pressure and the remainder was saponified. The saponification lye, when agitated with ether, proved to contain an unsaturated fluid acid. The analysis of its salts admits the inference that it contains 21 carbon atoms to the molecule. The acid as well as its ethylic ester, is characterized by its slight solubility in alcohol, so that it can be separated from the oil in the form of its ester without preceeding saponification by the removal of about 95 per cent of its more volatile parts, by distillation and by subsequent addition of alcohol to the remainder. The insoluble ester separates as an amorphous powder and can be obtained in a pure state upon repeated washing with alcohol. Its melting point is  $64^{\circ}$  to  $65^{\circ}$  and its odor a strong one of oranges. Further reports about this ester may be expected.

**Eucalyptus Oil.** On page 27 of our Report of October 1897 we mentioned the cultivation of Eucalyptus in Portugal. We meanwhile have received three specimens of oil obtained there.

1. Oil of *Eucalyptus rostrata* Schlecht. has a pleasant odor and a high amount of cineol; sp. gr. 0.921,  $\alpha_D = -1^{\circ} 8'$  at  $30^{\circ}$ ; soluble in 2 parts of 70 percent alcohol; renders no phellandrene reaction with sodium nitrite and acetic anhydride.
2. The botanic origin of sample 2 has not been determined and it remains to be ascertained whether the oil is obtained from *Eucalyptus resinifera* Smith or *Eucalyptus rostrata* Schlecht. After comparing it with the oil of sample 1, we deem it more likely to be derived from the former species. It contains cineol, as is shown by the iodine reaction, phellandrene and a terpene not yet found in the oil of *Eucalyptus rostrata*; its sp. gr. is 0.893, its angle of rotation  $\alpha_D = -17^{\circ} 8'$  at  $30^{\circ}$  and it is not soluble in 70 and 80 percent alcohol.
3. The oil of *Eucalyptus obliqua* L'Herit. contains, besides cineol, also phellandrene and is soluble in equal parts of 80 percent alcohol. Sp. gr. 0.914, angle of rotation  $\alpha_D = -7^{\circ} 28'$ .

In consideration of the surplus of good eucalyptus oils rich in cineol now in the market, the introduction of the two last named oils into commerce would have but slight chances of success. The oil of *Eucalyptus rostrata*, so far as the specimen at our disposal is concerned, may be considered equal to the better kinds of eucalyptus oils.

Messrs. R. T. Baker and H. G. Smith of the technological Museum at Sydney have reported<sup>1)</sup> on a new Australian eucalyptus oil derived from *Eucalyptus punctata* D.C. (*Eucalyptus tereticornis* Sm. var. *brachycoris*), called Grey gum. The tree also furnishes gum kino and a very hard wood. It grows in the entire coast-district of New South Wales, from Queensland to the borders of Victoria. The oil was obtained from the leaves and young twigs and represents the yield of nine distillations of material obtained from various localities. The yield of oil ranged between 0.63 to 1.19 per cent, its specific gravity between 0.9122 and 0.9205 at 17°. Two of the oils were laevogyrate ( $[\alpha]_D - 0.92^\circ$  and  $- 2.52^\circ$ ), the other seven dextrogyrate ( $[\alpha]_D + 0.54^\circ$  to  $+ 4.44^\circ$ ). An average sample of the various distillates had the following properties: Sp. gr. 0.915 at 16°, specific rotation  $[\alpha]_D = + 0.927'$ ; percentage of cineol determined by the phosphoric acid method<sup>2)</sup> 46.4 to 64.5. The oil contains no phellandrene.

Another as yet unknown West-australian eucalyptus oil has recently been described by Mr. E. J. Parry<sup>3)</sup>. It is obtained from *Eucalyptus toxophleba*<sup>4)</sup>, called "York gum" on account of its abundant growth in the neighborhood of the city of York. The oil has a very disagreeable odor, irritating the organs of respiration to vehement coughing. Its sp. gr. is 0.8828 at 15.5°, its angle of rotation about  $+ 5^\circ$ . Upon fractional distillation the following fractions were obtained: between 168° and 171°, 68 per cent; between 171° and 176°, 14 per cent; between 176° and 182°, 2 per cent; between 182° and 187°, 8 per cent; remainder, 8 per cent. The oil contains phellandrene and 15 to 20 per cent of cineol. Upon agitating the oil with bisulfite solution, it lost 20 per cent of its volume, indicating a considerable percentage of aldehydes and ketones. Amyl alcohol, shown to be contained to a small amount in the oil of *Eucalyptus globulus*, and to which the

1) On "Grey gum" (*Eucalyptus punctata* D.C.) particularly in regard to its essential oil by R. T. Baker and H. G. Smith. Journal and Proceedings of the Royal Society of N. S. Wales. Vol. 31, p. 259—280.

2) Whether the amount of cineol found may be considered correct, remains to be seen. Our efforts for the determination of the amount of cineol by the phosphoric acid process in oil mixtures of known percentage, rendered, quite unsatisfactory results.

3) London Pharmac. Journ. Vol. 61 (1898), p. 198.

4) This species is not mentioned either in F. von Müller's „Australian Plants", Melbourne, 1889, nor in Maiden's "Useful native plants of Australia", London and Sidney 1889.

irritating effect probably is due, could not be found in the oil of *Eucalyptus toxophleba*. The author expects to continue his researches.

At this opportunity we beg to call attention to some recently published essays on eucalyptus species with which we were favored by their authors: "On a new species of Eucalyptus from the Sydney-district" by Henry Deane, M. A., F. L. S. and J. H. Maiden, F. L. S. (Proceed. of the Linnean Soc. of N. S. Wales 1897, Part 3, Sept. 29.) and "Observations on the Eucalypts of New South Wales", III, by Henry Deane, M. A., F. L. S. and J. H. Maiden F. L. S. (Proceed. of the Linnean Soc. of N. S. Wales 1897, Part. 4, Nov. 24.)

**Fennel Oil.** The fennel cultivations in the neighborhood of Lützen and Weissenfels are in a good condition and a normal crop is expected. The crop in Galicia has been a good one too and the distillation is now in full play. A reduction of the price of fennel oil may be expected.

**Geranium Oil.** The abundant supply of fine grade oils continues. The number of plantations in Algeria has considerably increased and recently established distillers are adding perceptible competition to the older ones, cutting the prices to unprecedentedly low rates. It may be well for purchasers to take advantage of this chance.

Still less favorable are the affairs on Réunion where in consequence of the low prices the production has become unremunerative, suppressing any further interest in this industry. Moreover this oil in perfumery has recently lost a good deal of its former popularity on account of its peculiar properties when used in transparent soaps.

The fine Spanish distillate is still finding preference except in toilet soaps, where Algerian oil meets all requirement.

The supply of so-called Indian geranium or Palmarosa oil is somewhat difficult, inasmuch as the communication with the interior districts of the country has been much impeded by the prevailing pestilence in consequence of which the distillation on a smaller scale also has been curtailed. The orders for prime quality of oil, accumulated in Bombay, therefore, have been filled only in part and a number of exporters have been unable to meet their obligations.

A scarcity of good oil may occur before new shipments will arrive.

Messrs. Flatau and Labbé<sup>1)</sup> have published some notes on the acids of the geranium oils. They have found a saturated fatty acid  $C_{14}H_{28}O_2$ , melting at  $28^\circ$ .

In the course of years we have examined a considerable number of palmarosa oils of various origin and can state that no pure oil contains an acid with the properties mentioned. The French che-

<sup>1)</sup> Compt. rend. 126, 1876.

mists evidently have applied their examination to an oil sophisticated with cocos- or any other fat oil, as is well known, frequently met with.

The authors failed to find capronic acid, found in our laboratory some time ago to be contained in geranium oil. This may be due to the fact that they experimented with too small a quantity of the oil. It remains, however, incomprehensible how Messrs. Flatau and Labbé can surmise that we may have supposed a mixture of the fatty acid  $C_{14}H_{28}O_2$  and geraniol to be capronic acid. We cannot but accept that the authors have been unable to correctly interpret the essay of our chemists<sup>1</sup>).

Messrs. Flatau and Labbé found an oleic acid  $C_{18}H_{34}O_2$  in Réunion (Bourbon) oil of geranium, but failed to find tiglinic acid discovered by us in the oil years ago<sup>2</sup>):

**Guajacum Oil.** This splendid perfume, representing the pure odor of the finest tea more strikingly than any other, still continues not to meet with due appreciation by perfumers and manufacturers of fine toilet soaps. In their interest we once more beg to call their attention to this oil.

An effort to devise a practical method for the separation of the fluid part of the oil from the solidifying one has failed. The former remains fluid at a moderately warm temperature but solidifies upon repeated exposition to a cooler temperature. Since labor and care are unequal to the unsatisfactory results thus far attained we have for the present discontinued the manufacture of fluid oil of guajacum until better success in overcoming the technical difficulties will have been obtained.

The Bulgarian rose oil distillers have promptly recognised the value of guajacum oil, as more particularly reported on page 38.

After the statement in our Report of April 1898, p. 29, that the botanical origin of guajacum wood, called "*Palo balsamo*" in Argentina still has to remain an unsettled question, Dr. Paetzold of the Pharmaceutical Institute of the University of Strassburg meanwhile has informed us that he has ascertained the origin of the wood beyond doubt, by comparison with authentic specimens and by reliable information. The former statement<sup>3</sup>) that the wood is derived from *Bulnesia Sarmienti* Lor., a tree 40 to 60 feet high, belonging to the family *Zygophyllaceae* and closely related to *Guajacum officinale* L. has proved to be a correct one. According to Griesebach it is indigenous in the Argentine provinces of Oran and Grande Chaco, particularly along the course of the river Rio Bermejo, a branch of the Rio Paraguay.

<sup>1</sup> Schimmel & Co.'s Report, April 1896, pp. 34—37. — Arch. d. Pharm. 234, p. 326.

<sup>2</sup> Schimmel & Co.'s Report, April 1894, p. 31. Barbier and Bouveault, Compt. rend. 119, 283.

<sup>3</sup> Schimmel & Co.'s Report, April 1898, p. 28.

The wood is shipped from Buenos Ayres and has recently been thrown upon the markets in quantities far exceeding the demand for its oil in perfumery. Unless some other application of the oil on a grand scale is found, the importers will have to suffer from a further excessive supply of the wood, even if the use of the oil for perfumery purposes should increase tenfold over its present consumption.

**Hop Oil.** Persistent rains in May and June and subsequent long continued heat and drought have much impaired the crop of hops in Germany this season. In some localities the so-called "copper brand" has infected and much injured the plants and the crops. The harvest, therefore, is estimated to be less by one quarter than that of last year.

Since the stock left from last year is rapidly being used up, a rise of prices is expected; it will, however, not reach as high figures as dealers and speculators anticipate in their interest. In this respect the weather during the pending harvest will be of considerable influence, as also the reports on the crops in Great Britain and America. The trade in so-called "early hops" has already commenced.

**Juniper-berry Oil.** The new crop of berries is anticipated with some anxiety, since the last year's supply of Italian berries which were almost exclusively at our disposal, was of a very inferior quality, so much so that the oil was a product by no way up to the standard of a normal one.

The present crop of juniper berries in Hungary is of the best quality; we expect shipments this month and shall start the distillation at once on the receipt of fresh fruits. We are ready to receive larger advance orders for our own fine distillate.

In Italy also the crop has been a good one.

The new British pharmacopœia assumes oil of juniper berries to be obtained from the fullgrown green unripe fruit. This is an error, at least no such oil is distilled on a large scale. It is an antiquated idea, originating with Zeller, that unripe fruits render a larger yield in oil than ripe ones. In any case, the oil distilled from unripe berries in all essential qualities is inferior to the normal oil of ripe fruits.

The same pharmacopœia states oil of juniper berries to be soluble in four times its volume of a mixture of equal parts of 90 percent alcohol and of absolute alcohol. This statement is also not quite correct inasmuch as only freshly distilled oil has this quality. Within a few weeks it loses this degree of ready solubility and renders a very perceptible turbidity with four times its volume of 95 percent alcohol.

**Lavender Oil.** We have received the following reports from the different French departments which contain the principal lavender fields:—

**Départements des Alpes maritimes et Basses Alpes.** After an abundant flowering of the plants subsequent persistent drought has acted unfavorably and caused a smaller yield of oil. The total result, however, has been a better one than last year. Nevertheless higher rates are asked but as yet not accepted by purchasers because they are considered to be unjustified. The supplies of new oil have still the so-called "fresh herb" odor but seem to be of good quality.

**Département du Hérault.** Here matters are said to be much less favorable. The persistent drought during the early part of the summer has much retarded the normal development of the plants and there can be no doubt that the total yield of the lavender distillation of this year will remain behind that of last year.

**Département du Drôme.** In consequence of unfavorable weather conditions the production of oil of lavender will be an insignificant one in the northern districts of this province, one of the most important ones for the lavender industry. Repeated hail storms have devastated the lavender fields much. The eastern districts have suffered from a persistent drought for more than two months. In many localities no laborers could be obtained for harvesting the plants, much retarded in their development and often not worth transportation. The yield of oil, of course, is but a slight one and high prices are anticipated.

**Département du Gard.** The abnormal drought has here also damaged the plants very much. The total crop is estimated to be about half as large as last year and prices of 18 to 20 francs per kilo are anticipated. They will, however, hardly reach this rate, since the oils of this department generally are wanting in linalyl acetate, rarely surpassing 30 per cent.

Although these reports would justify higher rates for this important oil, prices have declined in the last weeks. We have secured ample stock of the two first-class grades of lavender oil and are in position to furnish oils of unsurpassed quality at very low figures.

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We have received from Portugal a specimen of oil of lavender obtained from *Lavandula pedunculata* Cav., indigenous on the Iberian Peninsula. Its odor is rather indistinct and not pleasant so that the oil hardly is of any use for perfumery purposes. Its specific gravity is 0.939, its optical rotation  $\alpha_D = -44^\circ 54'$ , and it is soluble in equal volumes of 80 percent alcohol. Its high figure of saponification, 111.7, corresponds to 39 per cent of the acetic acid-ester of an alcohol  $C_{10}H_{18}O$ . Upon distillation of the saponified oil with steam, a light-yellow liquid passed over. The first fraction contains cineol as is shown by the cineol-iodol-compound. The odor of this fraction is indicative of the presence of thujon besides that of cineol.

**Lemongrass Oil.** The sales of available stock were limited, and the rates fluctuating during the summer season. Orders for delivery in October and November at 4 d. down to  $2\frac{1}{4}$  d. were placed in CochinChina, but the latter rate was evidently nothing but

a feeler remaining in fact without a practical result. Most contracts were concluded upon the basis of  $2\frac{3}{4}$  to 3 d., equivalent to *M* 8.50 to *M* 9.50 per kilo.

The present commercial position of this commodity seems to be the following: Only a part of the large quantities of oil imported last season has been disposed of for use; another part has been purchased by speculators in London while the prices were rising, in the hope of a pending boom and great profits. This hope has not been realized, they have their stock on their hands and are reluctant to dispose of it at a loss. In Cochinchina too a number of native speculators has made the same venture and is now interested in a maintenance of high rates. This they will be able to do only until the shipments of oil of the new crop will arrive, probably in December. The fact may also be taken into consideration that under such favorable chances the producers generally enlarge their cultivations in the hope of ready and profitable sales and that, therefore, an exceptionally abundant supply may reach the present markets.

It is said that this all around speculation was largely sustained by the expectation that great quantities of lemongrass oil would be required for the manufacture of ionone. However considerable the amount of oil used for this purpose may be, the immense diffusive power of ionone limits its manufacture and consumption so that the application of lemongrass oil for this purpose is not large enough to exercise anything but an insignificant influence on its general consumption, particularly as the annual total production reaches at least 3000 cases or about 21,000 kilos.

It is therefore not advisable at present to lay in any excessive stock of the oil.

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*"Bulletin of miscellaneous information Royal Gardens Kew"* No. 140, page 206, contains the statement that the interest in the cultivation of lemongrass and the production of oil recently have relaxed in the Straits Settlements. The remark that the grass is *Andropogon Nardus* L. is contrary to the general opinion sustained by Flückiger and Hanbury (*Pharmacographia*, page 725) and by Dymock (*Pharmacographia Indica*, Vol. 3, page 564) that *Andropogon Nardus* L. supplies citronella oil and *Andropogon citratus* D. C. lemongrass oil. An explanation would be interesting whether the statement in the *"Bulletin"* is based upon recent botanical enquiries, or whether a mistake in the names of the plants has been made.

**Linaloe Oil.** During the last six months the prices of this oil have experienced considerable fluctuations but have finally acquired a normal basis, inviting to an ample supply without any risk.

We have again come across several adulterated oils, and in one case of a "direct" import, the cans were found to be filled half

with water, while the oil floating on the top proved to be of unexceptional quality. In sampling the oil the tests were made with the oil on the top, the water below was not noticed until the cans were emptied.

**Marjoram Oil.** Our knowledge of the constituents of this oil was mostly of older origin and fragmentary. A recent examination of the oil by Mr. W. Biltz<sup>1)</sup>, guided by Professor Semmler, in the laboratory of the University of Greifswald has shown it to contain terpinene and d-terpineol while the effort to isolate the characteristic odoriferous principle for the present failed.

The assertion made in the essay that d-terpineol as yet had not been noticed in oils, should be corrected so far, as this substance has previously been found in our laboratories as a constituent of lovage- and of Malabar cardamom oils<sup>2)</sup>.

**Matico Oil.** Recent shipments of matico leaves show a much better quality, much richer in oil than those before. Matico oil can now again be supplied in large quantities at fair prices.

In the distillation of matico oil we have made the conclusive observation that commercial matico—a mixture of leaves and spikes—not always is of uniform origin. Appearance and odor do not show any considerable differences, but the distillates do so, particularly in their physical properties. These are not due to variations in the relative amount of spikes admixed to the leaves. Since some time the distilled oils fail to yield the characteristic crystallizing matico camphor. From one oil ( $d_{15}^{20} = 1.077$ ;  $\alpha_D = -0^\circ 25'$ ) we obtained, after repeated recrystallization from petroleum ether, a solid substance melting at  $62^\circ$ , which proved to be asarone. Upon combining with one molecule of bromine in petroleum ether solution, the addition product asarone bibromide was obtained in crystals melting at  $85^\circ$  to  $86^\circ$ . When oxidized by potassium permanganate asarylic acid melting at  $144^\circ$  was formed, characterized by its argentic salt.

**Mirban Oil.** The prices of this commodity have reached the lowest possible minimum rates. The customary criterion of its quality is the so-called "lye test". The lye has to remain uncolored when boiled for some time with oil.

**Neroli Oil, synthetical, "Schimmel & Co."** The superiority of this exquisite product meets with increasing appreciation. Any further recommendation would be amiss, if the circle of the readers of our Reports was not constantly on the increase. This fact necessitates in some instances and on particular occasions a repetition of statements of practical importance.

<sup>1)</sup> Inaug. Diss. Greifswald 1898.

<sup>2)</sup> Schimmel & Co.'s Report, April 1897, p. 27, and October 1897, p. 11, and Note 3.

Fortified by constant observations made since the year 1895. with perfumes of all possible varieties, we can affirm that our synthetic neroli has fully sustained the high expectations in every way. All the various compositions in which it has been employed emit the pure odor of orange flowers rather stronger than those scented with the natural oil. This fact was noticed and recognized by experts.

It is comprehensible that such a product meets the antagonism of the competing producers of the French oil, but the fact remains undeniable that synthetic neroli is at least equal to the best natural oil. The constantly increasing demand for and use of it is the best proof that its superiority is being recognized more and more. An additional evidence of this fact consists in the noticeable influence of our product upon the prices of the natural oil, which would rate far higher at present, if it were not for the potent competition exercised by synthetic neroli.

In recommending our product to the most critical examination and to due application in perfumery, we beg to call to mind the fact that the same is stronger in fragrance by about 10 per cent than the natural oil.

**Orris-root Oil.** The anticipation of Italian producers has not been realized. The expected rise of prices has not occurred and the alleged speculative purchase of all available stock of the oil by some American firms has proved to be nothing but moonshine. It becomes more and more evident that a clique of speculators is at work to corner this commodity and that they are not very scrupulous in the means they choose for attaining their object.

It is alleged in Florence and the producing districts of the root that the present crop has been a smaller one than that of last year. Nevertheless, the prices remain stationary, but a rise by at least 25 per cent is predicted to take place as soon as the combine in Florence has settled its program of action. This is based upon the following speculation:—

Yield of the crop of 1897 . . . 1,300,000 kilos

Stock remaining from the year 1896 500,000 „

---

1,800,000 kilos.

It is alleged that this quantity nearly has been disposed of. In case the crop of this year should prove as large as that of last year, only 1,300,000 kilos would cover the entire available stock; that is one third less than the consumption of the last year amounted to. These calculations possibly may approach correctness, but the fact is left out of consideration that immense quantities of root have been bought on speculation last year, and that in consequence a number of prominent consumers are provided with a sufficient stock so that they will have little need for resorting to the market in roots.

As the crop of this year appears to be a normal one it will be prudent not to rush to new purchases and that the less as it is very likely that considerable quantities of roots from the year 1897 are still in stock in Italy. The harvest of this season has been favored by fair weather conditions. The rhizoms are fine and of a strong aroma.

The present prices of orris oil are calculated upon the lowest possible rates of the value of the roots. The oil cannot be supplied in a pure and fine condition at a lower price. We recently came across an orris oil, whose fragrance evidently had been enhanced by the addition of a well known synthetic product, very probably identical with the so-called sapirone. Such an oil captivates by a winning and strong odor, foreign, however, to a true and pure distillate of the root as well as to pure irone. We feel justified to call attention to this observation, because otherwise perfumers might be induced to experiment with such doctored oil.

Sapirone will soon be introduced into the market, as may be seen on page 62 of this Report.

**Patchouli Oil.** The supply of good Penang leaves in Singapore was relatively as considerable as that shipped directly to Europe. Several of these shipments remained unsold for quite a time and finally were disposed of at any price. The penetrating and persistent odor of the drug has brought it into disfavor in all public storage houses, as likewise with shippers.

A fine patchouli oil is indispensable in perfumery and at the present low prices there is no drawback to a most liberal use of the oil.

**Peppermint Oil, American.** According to information obtained by our New York branch, the yield of peppermint in the State of New York is by about 25 per cent below that of last year's crop. The plants first suffered from frosts and later on from want of rain, in some localities even from drought.

Still less favorable are the reports from the districts further west. The shortage of this season is estimated there, according to the location of the fields, at 30 to 50 per cent. The great care and labor required in the cultivation of peppermint has been in vain on many farms. One of the largest farmers in Decatur, who had planted 90 acres with new plants, notwithstanding this addition to his fields in cultivation, obtained only 8000 lbs. this year against 11,000 lbs. last year. The farmers in some districts got about 12 lbs. of oil from each acre of land, those in other about 15 lbs. In the peppermint raising districts the opinion prevails that the present yield of oil will not satisfy the demand. Whether this view is correct, depends on the amount of stock still kept in store. So far the market prices have been but slightly affected; it therefore seems that discouraging reports encounter scepticism. But there can hardly be

any doubt that oil of peppermint will eagerly participate in speculation, in case a "boom" should occur in the general business of the United States.

**Peppermint Oil, English.** The peppermint crop has failed to realize the expectations in the Mitcham district as well as in Lincolnshire, the weather conditions having been unfavorable throughout the summer. The crop proves deficient in oil; in consequence the prices at the beginning of the harvest are higher by about 25 per cent this year than last one; a price of 30/ per English pound is anticipated and some producers still defer all sales.

We have laid in our annual stock amounting to about 7000 lbs. and have accordingly fixed our rates. But in the course of time a rise of rates may become unavoidable.

This of course refers only to pure original distillates of reliable origin and not to the products of dealers who meet any demand as to quality by the admixture of Japanese oil. Mitcham peppermint oil is *par excellence* an article of implicit trust.

**Peppermint Oil, Japanese.** In consequence of the persistently ruinous prices the cultivation of peppermint is said to have been largely reduced in the Yonezawa and the Bingo-Bitchin districts. The yield of the first cut is estimated at about 7000 and of the second one at 13,000 catties, together about 20,000 catties.

This would amount to less than half the crop of last year. On the other hand, the stock of available oil is said to amount to about

6,000 catties . . . . .	in Bingo-Bitchin
70,000     "     . . . . .	"     Yonezawa

and these estimates are considered to be rather too low. Compared with the results of the preceeding years, the following figures are instructive:—

1896: yield and stock in oil about	223,300 catties
1897:     "     "     "     "     "     "	140,000     "
1898:     "     "     "     "     "     "	100,000     "

The report is also of interest that experimental plantations of peppermint have been instituted upon the most northern island of the Japanese Empire, Hokkaido (Yesso). The yield of oil of the present harvest is estimated at 500 catties.

In order to form an idea about the rates of the pending peppermint markets it is of paramount importance to obtain correct estimates about the stock in oil, both in Europe and America. The principal port of importation and market on the continent is Hamburg. The imports of Japanese oil amounted there in:—

1896 . . . . .	to 24,000 kilos
1897 . . . . .	" 30,470     "

In consideration of the dull business in oil, the conclusion may be justified that a large stock has accumulated in Hamburg.

The present rates for the three kinds of Japanese peppermint products in commerce, namely liquid dementholized oil, normal oil containing 40 to 50 per cent of menthol, and crystallized menthol, may be considered the cheapest possible ones. The Japanese claim not be able to afford any further decline and we cannot but concur in this view.

**Peppermint Oil, German,** of our own cultivation. Our fields in the neighborhood of Leipzig have this year yielded a normal average crop both in herb and in oil. The second cut, gathered early in September, was also a good one. The distillate of the present year is of exceptional fine quality. We have also considerably extended our plantations this year.

**Pine-needle Oils.** As is to be seen in our Price List, we again can supply an extra-fine quality of the oil from the young cones of *Abies pectinata*. This oil could not be distilled last year, because the cones had been prematurely knocked off by vehement storms. Many of our customers will be glad to be again able to obtain this fine oil. The Siberian pine-needle oil is more and more meeting with favor; it is a pure distillate, rich in bornyl acetate and in consequence very far reaching in its odoriferous power. The oils from *Pinus pumilio* Haenke, and from the needles of *Abies pectinata* D.C. in pure original distillates are as usual in stock.

**Rose Oil, Bulgarian.** The rose crop, impaired by less favorable weather conditions, has yielded a smaller production of oil than last year. It amounted in the several districts as follows:—

Kazanlik . . . . .	485	kilos
Karlovo . . . . .	740	„
Bresovo . . . . .	215	„
Pechtera and Plovdio . . . . .	85	„
Ovtchehlmi . . . . .	48	„
Stara-Zagora . . . . .	52	„
Nova-Zagora . . . . .	45	„
Tschirpan . . . . .	50	„

total: 1720 kilos

against 2403 kilos in 1897

and 3517 „ „ 1896.

The export amounted, according to a statement in the June number of the "Deutsches Handelsarchiv", in:—

1897 to 3192 kilos of rose oil (583 kilos exported to Germany)  
 1898 „ 3312 „ „ „ „ (693 „ „ „ „ „).

These figures are in excess of the production of Bulgarian oil, if the reserve stock remaining each year is taken into consideration. The figures therefore are suggestive as to the whereabouts of the excess.

When the considerable stock remaining from the last two years is added to the 1720 kilos of the yield in oil of the present year, it cannot but surprise that the price nevertheless has considerably declined. This is additional evidence of the utter demoralization of the Bulgarian rose oil industry and of the fact that the trust in "pure oil of roses" has vanished in the purchasers. At the rate of *M* 600 to *M* 680 per kilo paid for "best" Bulgarian rose oil this season, no pure oil can be procured and the inference is justified that the "doctoring arts" in the rose oil production must have been in full sway this year, notwithstanding all ordinances against their practice.

As already mentioned in regard to oil of guajacum wood on page 29, this oil seems to have been promptly recognized by Bulgarian rose oil producers as a novel and convenient adulterant. We have recently come across a sample of Bulgarian rose oil which by its odor at once was discovered to consist of guajacum oil somewhat modified by an admixture of geranium oil. Guajacum oil, as is well known, has the property of solidifying with a fine crystalline structure at ordinary temperatures. It consists mainly of an alcohol, melting at  $+ 9.1^{\circ}$ . This fact evidently has inspired some smart compounder to utilize this property of the oil for restoring the strong tendency to crystallisation of those geranium oil substitutes for rose oil whose degree of solidification has been impaired by too considerable an admixture of this traditional adulterant. The property of readily solidifying is still considered an imperative criterion of quality in Bulgaria. This desideratum is embodied in guajacum oil, and its mild tea-like odor can well be blended with that of rose oil so that such an admixture is not easily noticeable, even when made in a considerable proportion.

**Rose Oil, German.** We are sorry to state that this year's crop has remained considerably behind the yield of last year. This want of success, however, was not due to unfavorable weather conditions but to a mistake made in some of the intricacies of the rose culture.

The cool and damp weather of the early summer was favorable to the plants; flowering set in slowly and gradually, greatly facilitating the plucking of the flowers. They were, however, deficient in oil. The total yield of fresh flowers amounted to about 145,000 kilos. The gathering commenced June 15<sup>th</sup> and ended July 20<sup>th</sup>, making in all 36 days and yielding on the average 4000 kilos per day.

Part of the fields received new plants last year and, provided that normal weather conditions will prevail, we expect to again attain to the normal crop of about 250,000 flowers next season.

**Rosemary Oil.** In consequence of an abundant yield of the distillation, Dalmatian, also called Italian, oil of rosemary has declined

in price. The use of pure oil seems to be influenced by the gross adulteration practised with this oil. A reaction may be expected to take place in Germany as soon as our request made to the proper authorities will be granted that pure rosemary oil only be admitted for the denaturation of fatty oils.

The French oil ranges somewhat higher in price. The plants have been damaged in the producing departments with the exception of that of Du Drôme and in some localities even ruined by persistent droughts. It is apprehended that the oil will become scarce and rise in price during the present year. Oils responding to the most exacting qualification, namely that of not rendering any dextrogyre rotation in the first 10 per cent of the distillate, are very scarce. Most specimens submitted to our estimate contained admixtures of French oil of turpentine.

**Sandal-wood Oil.** By sharp competition the prices have been cut to such an extent, that a remuneration commensurate to the troublesome production of this oil is not obtainable any more. The values of the respective kinds of wood has also remained stationary and the Mysore Government takes particular care to prevent any further decline of values. The system till now prevailing of assorting the wood, has been altered this June, and already the next December-auction will be conducted in accordance with the following new

#### Revised Official Classification of Mysore Sandalwood.

- I. **First Class Billets** (or Vilayat Budh). Consists of thoroughly sound billets weighing not less than 20 lbs. and not exceeding 112 pieces to the ton.
- II. **Second Class Billets** (or China Budh). Consists of slightly inferior billets weighing not less than 10 lbs. and not exceeding 224 pieces to the ton.
- III. **Third Class Billets** (or Panjam). Consists of billets having small knots, cracks and hollows, weighing not less than 5 lbs. and not exceeding 448 pieces to the ton.
- IV. **Chotla** (or billets of short length). Consists of short sound pieces no limit as to weight or number.
- V. **Chat Badala**. Consists of billets with knots, cracks and small hollows at either end, weighing not less than 10 lbs. and not exceeding 240 pieces to the ton.
- VI. **Bagaradad**. Consists of solid pieces without limit as regards dimensions weight or number.

N. B.—Billets of Classes V and VI are not planed nor are their edges rounded off.

- VII. **Roots** (first Class). Consists of pieces weighing not less than 15 lbs. and not exceeding 150 pieces to the ton.
- VIII. **Roots** (second Class). Consists of pieces weighing not less than 5 lbs. and not exceeding 448 pieces to the ton.
- IX. **Roots** (third Class). Consists of small and side roots below 5 lbs. in weight.
- X. **Jugpokal** (first Class) or Badala. Consists of hollow pieces weighing not less than 7 lbs. and not exceeding 320 pieces to the ton.

- XI. Juggokal (second Class). Consists of hollow pieces weighing not less than 3 lbs.
- XII. Ain Bagar. Consists of solid cracked and hollow pieces weighing not less than 1 lb.
- XIII. Cheria (or large Chilta). Consists of pieces and chips of heartwood weighing not less than  $\frac{1}{2}$  lb.
- XIV. Ain Chilta. Consists of pieces and small chips of heartwood.
- XV. Hatri Chilta. Consists of heartwood chips and shavings obtained by planing.
- XVI. Milwa Chilta. Consists of pieces and chips having in fair proportions heartwood and sapwood.
- XVII. Basola Bukni. Consists of small heartwood and sapwood chips.
- XVIII. Saw dust or Powder. Obtained in sawing the sandalwood.

Moreover, the Mysore Government has refused to extend to a native concern the privilege of exclusively distilling sandal-wood oil in India for a term of ten years, a previous monopoly having terminated in 1896. It appears that the Government intends to engage upon the distillation itself in case no party should be ready and able to enter upon this work with modern machinery and appliances at its own expense and risk without obtaining a monopoly. In consideration of the present unprofitable prices of the oil it would in our opinion, be hazardous if not folly, to risk the considerable capital requisite for the erection of a modern plant for the production of sandal-wood oil.

Besides, the distillation of sandal-wood oil has recently been commenced in Fremantle in Western Australia, where the so-called Swan river wood is obtained in an abundant supply. We were the first to distill this wood in the year 1875, but observed at once that the oil obtained therefrom was inferior to the East Indian oil. But for this fact we certainly would have taken into our hands the distillation of the Australian wood, being much prompted to do so. This wood is derived from *Santalum cygnorum* Miquel, the East Indian from *Santalum album* L.

We are waiting for original specimens of the Australian oil ordered for the purpose of ascertaining whether a considerable difference exists in the percentage of sandalol contained in this oil compared with the oil of the East Indian wood.

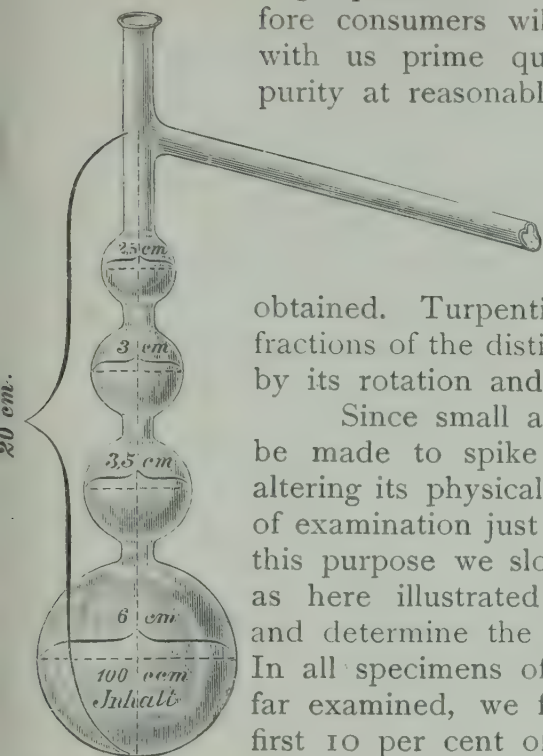
**Spike Oil.** The same holds good for this oil as has been said of lavender oil on page 31. The yield was deficient, particularly in the Departements Drôme and Gard, where the plants had suffered from drought and subsequently by fogs and, moreover, had been disposed of at high rates in the expectation that the high prices of last year, amounting to Frs. 9 to 10, would also prevail this year. At the fair held September 9<sup>th</sup> at Le Vigan, Gard, the farmers asked as much as Frs. 8.— per kilo, a price which the firms represented were shy to invest. We have purchased on delivery and at fair rates

large quantities of the oil some months ago. Therefore consumers will have no trouble in obtaining with us prime qualities of spike oil of absolute purity at reasonable prices.

In the examination of lemon- and rosemary oils for an admixture of turpentine oil, we distill part of the oil and determine the optical rotation of the distillate

obtained. Turpentine oil passes over with the first fractions of the distillate and can readily be identified by its rotation and specific gravity.

Since small additions of oil of turpentine may be made to spike oil without thereby perceptibly altering its physical constants, we apply the method of examination just mentioned to spike oil also. For this purpose we slowly distill in a fractionating flask as here illustrated 5 Cc. of the oil from 50 Cc., and determine the angle of rotation of this fraction. In all specimens of spike oil of reliable origin thus far examined, we found dextrogyre rotation of the first 10 per cent of the distillate:—



Specific gravity	$\alpha_D$	Solubility in 70 percent alcohol	$\alpha_D$ of the first 10 per cent
1. 0.916	+7° 7'	1:3	+7° 11'
2. 0.915	+7° 3'	1:2	+5° 10'
3. 0.914	+5° 0'	1:2.5	+7° 11'
4. 0.918	+5° 30'	1:2.5	+6° 7'

If a small quantity of French oil of turpentine should be admixed to such oils, they would still answer the requirements of our former test, but the rotation of the first fraction of 10 per cent would become laevogyre.

Our criterion of pure oil of spike was so far:—

1. Specific gravity not below 0.905;
2. Dextrogyr rotation;
3. Solubility in 3 parts of 70 percent alcohol.

We suppose, however, that this limit of specific gravity is estimated rather too low and shall pay special attention to this point, henceforth exercising due consideration of the results of distilling the oil.

In order to obtain correct results for comparison, uniform flasks should always be used and the distillation carried on in such a way that about one drop of distillate is obtained in every second. We now use exclusively Ladenburg's fractionating flasks corresponding in dimensions to the above illustration.

**Star-anise Oil.** The price of this important commodity has been influenced but little by the revolution in the Provinces of Kwang-Si and Kwang-Tung, the centres of the Chinese star-anise production. The rates would perhaps have more risen, if the French Colony of Tonkin had not been able to supply any deficiency of oil in the markets. Meanwhile efforts have been made in China, induced by the French competition, to counteract the prevailing systematic practices of adulteration. The custom-house at Lungchow issued a recommendation, February 16<sup>th</sup> 1898, that arrangements should be made of having all shipments of oil going to Pakhoi-Hongkong closely examined at Lungchow in order to stop adulterated oils from passing on to Hongkong. If this practice were not prevented in time, the producers would sell their good oil to Langson (Tonkin) and the adulterated oil to Pakhoi and Hongkong. This would be equivalent to degrading the latter port to an emporium of second class merchandise in star-anise oil.

Messrs. Melchers & Co. in Hongkong hereupon felt induced to vigorously push this matter. They have by our aid purchased in Germany a large number of the apparatuses for the determination of the point of solidification of the oil as also a machine for artificially making the requisite ice, and have sent them all to Lungchow. There is reason to hope that all appliances requisite for the examination of star-anise oil at present are in full sway in Lungchow and the principal Chinese emporium Pos-Seh, and that unobjectionable oils with a high solidification point will soon reach Hongkong.

By the favor of the above named firm we have recently obtained five samples of oil said to be distilled from the flowers of the star-anise tree. They seemed to be pure but showed strikingly low points of solidification. Their properties were:—

	Opt. rot.	Sp. gr.	Solubility	Solidification point
No. 1:	+0° 11'	0.998	in 1½ Vol. 90 percent alcohol	+ 8¾°
„ 2:	+0° 18'	0.988	„ 1½ „ 90 „ „	+ 13½°
„ 3:	+0° 32'	0.991	„ 1½ „ 90 „ „	+ 13¼°
„ 4:	+0° 26'	0.990	„ 1½ „ 90 „ „	+ 13½°
„ 5:	+0° 26'	0.991	„ 1½ „ 90 „ „	+ 13¾°

From these figures the oils cannot be considered to be of normal quality, although their purity may be beyond doubt. The samples kindly sent were unfortunately too small to admit the determination of the constituents to which the decrease of the solidification point is due. We expect, however, soon to receive larger quantities of these oils and then to clear up any doubts about their constituents.

Meanwhile we append the following report on star-anise oils received from Langson (Tonkin):—

The principal gathering of the star-anise crop begins in July and ends in October; besides this, two additional but smaller crops are obtained, one in January and February, the other in March and April. The oil distilled from these two crops is called *Tu-qui* oil (Flower oil) or more correctly *Noa-tu-qui*

(Flowers of the four seasons). This oil is, however, not at all obtained from the flowers, but by distilling the early fruits long before they attain to full ripeness. The premature removal of a part of the unripe fruits is said to be a necessity and a relief to the trees to facilitate the ripening of the rest of the fruits.

The oils distilled from unripe fruits, although considered in Tonkin to be of a finer aroma, cannot well be accepted as marketable.

The annual star-anise oil production amounts, according to an estimate by Mr. H. B. Morse, Collector of Customs at Lungchow:—

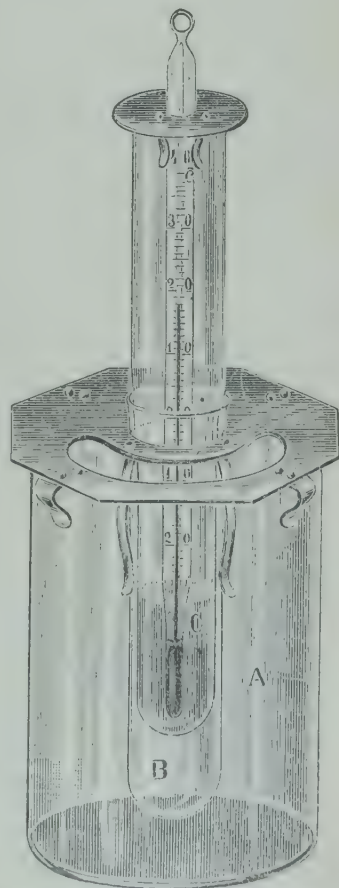
in the district of	Pos-Seh	in China	to	1500	piculs
" "	" "	Lungchow	" "	500	"
" "	" "	Langso	" Tonkin	500	"

Total 2500 piculs

= 5000 cases or 150,000 kilos.

It affords us a pleasure to be able to append to this Report a map of the Tonkinese star-anise districts. For the skeleton of the same we are indebted to Mr. J. L. Simon of Paris, as well as to his representative in Hanoi, who are deserving of great credit for their energetic and successful efforts in clearing the ignorance prevailing until a few years ago in regard to the sources and the production of star-anise oil.

For the determination of the point of solidification of essential oils, the well-known Beckmann's apparatus for the determination of the molecular weight from the decrease of the freezing point may well be used. A few small modifications make it particularly suited for the examination of anise- and star-anise oils. These slight alterations consist mainly in the removal of the cork-connections, by which the full view of the mercurial column of the thermometer was impeded. The lateral branch of the freezing tube C of the Beckmann's apparatus, serving for the introduction of the substance to be examined, can also be missed. The following illustration explains the apparatus as modified by us for our purpose. The battery jar A serves for receiving the refrigerating fluid. The test-tube B suspended in the metal cover serves as aircover around the freezing tube C, preventing the premature solidification of the oil to be examined. This tube is wider at its top, narrowing down at the junction where it rests on the rim of the lower tube B. In order to support the tube C in the tube B, three glass protuberances are affixed on its inside about



One fourth of the natural size.

5 Cc. below its upper rim. The thermometer, divided into  $\frac{1}{2}$  degrees, is supported in a metallic cover by three small springs, permitting a ready displacement both upwards and downwards.

For making the determination for anise and star-anise oils, the jar is filled with iced water and broken ice, for fennel oil with a freezing mixture consisting of broken ice and common salt. Then the sample of oil to be tested is introduced into the freezing tube C reaching to a height of about 5 Cm. and the thermometer is inserted into the oil with the precaution not to touch the wall of the tube in any place. During the cooling-process any concussions have to be avoided as they tend to cause a premature solidification of the oil<sup>1</sup>). When the thermometer has reached about  $10^{\circ}$  below the point of solidification, this being at  $6^{\circ}$  to  $8^{\circ}$  for anise- and star-anise oils; the solidification is induced by gentle friction with the thermometer upon the wall of the tube holding the oil. Should this simple procedure fail of its object, a minute crystal of solidified oil or of anethol may be introduced into the fluid, whereupon the crystallization sets in at once, disengaging considerable heat. It may be accelerated by constantly stirring with the thermometer, whose mercurial column rapidly rises, soon reaching the maximum height, called the point of solidification of the oil.

**Valerian Oil.** The remaining stock is being gradually disposed of. New supplies will command higher rates.

**Wintergreen Oil.** Natural oil of wintergreen contains, as is well known, as principal constituent methyl salicylate, whose percentage can readily be determined by the saponification process by means of alcoholic potassa solution of a known strength. For the same purpose, Professor Kremers and Miss Martha James<sup>2</sup>) propose for the determination of salicylic acid in the saponified oil a method advanced some time ago by Messrs. Messinger and Vortmann. This consists in converting the salicylic acid in the presence of a surplus of alkali by means of a iodine solution of known strength into diiodo-salicylic acid, and determining the amount of iodine remaining uncombined by titration with deci-normal thiosulfate solution. Even in consideration of the fact that the oils both of *Betula lenta* and *Gaultheria procumbens* contain small amounts of various esters different from methyl salicylate, which upon saponification also pass as methyl salicylate, this slight deviation from exact results will not be considered unsafe in the determination of the total amount of methyl salicylate by means of the saponification method, because

<sup>1</sup>) A premature solidification may also occur when the oil is not perfectly free from any suspended particles, as happens when it has not been completely cleared by previous filtration. The method of examination rests upon the property of anethol of becoming cooled considerably below its freezing point without solidification.

<sup>2</sup>) Pharmac. Review, Vol. 16 (1898), p. 131.

it is by far simpler and more practical than the method recommended by Professor Kremers and Miss James.

Dr. van Romburgh<sup>1)</sup> of the botanical Garden at Buitenzorg on Java has recently furnished additional proof of the wide distribution of methyl salicylate in the vegetable world. Of 900 various plants examined for volatile constituents, 160 or 18 per cent rendered a distillate containing more or less of this ester. None of the distillates furnished the methyl salicylate reaction when the plants had been distilled the day when plucked, but did so when distilled one day after. This observation sustains the inference made by Messrs. Bourquelot, Schneegans and Gerock some time ago that methyl salicylate is fixed in the plants as a glycoside compound.

Dr. van Romburgh found methyl salicylate most frequently in plants of the family *Leguminosae*, but also in one or several species of the families *Aurantiaceae*, *Celastrineae*, *Compositae*, *Cupuliferae*, *Ebenaceae*, *Euphorbiaceae*, *Gramineae*, *Jasmineae*, *Lonicereae*, *Meliosmeae*, *Myrtaceae*, *Olacineae*, *Polygaleae*, *Rhamnaceae*, *Rosaceae*, *Rubiaceae*, *Sapindaceae*, *Staphyleaceae* and *Tiliaceae*. The ester is contained sometimes only in one or more organs, sometimes in all parts of the plant. As yet nothing is known of what part methyl salicylate plays in the vital processes of plants.

In our Report of April 1898, on page 52, there is contained a list of plants, republished from an essay by Professor Kremers and Miss Martha M. James, enumerating those plants in which methyl salicylate thus far had been discovered. The late Dr. de Vrij briefly before his demise called our attention to a slight misstatement; as the discoverer of methyl salicylate in *Gaultheria punctata* and *G. leucocarpa* the name of Köhler is stated. This is an error, as Dr. de Vrij had observed the ester in these plants many years before. De Vrij caused Mr. Köhler to submit the distilled oils of both plants to a closer examination, and in consequence Köhler has ever since been mentioned as originally having observed the presence of methyl salicylate in plants. Dr. de Vrij's observation was published in the year 1871 in the *Pharmac. Journ. and Transactions* (3) 2, page 503.

**Ylang-Ylang Oil.** The production of this oil was completely stopped upon the Philippine Islands during the last 6 months by the war between Spain and the United States. It now remains to be seen how much the plantations have been devastated by the war, and whether it will be possible to again take up the gathering and the distillation of the flowers at the time of blooming in October. Since the principal oil industry is carried on in the neighborhood of Manila the damage may be a considerable one.

<sup>1)</sup> From a reprint of the Proceedings of the Academy of Sciences at Amsterdam, kindly sent by the author.

Notwithstanding the stoppage of all shipments from Manila during the time of the blockade, no scarcity of oil has thus far been felt. The stock accumulated in the principal markets has sufficed to cover the demand. In case the production and the shipment of oil can be taken up again soon, no crisis in this commodity will take place. Should this, however, fail to occur, a want of oil may be felt during the coming winter. In this case synthetic oil of ylang-ylang of great excellence manufactured by us will come into prominence and will no doubt meet with deserved appreciation. With many perfumers it has found favor and preference. It has, besides, the advantage of securing to the arts of perfumery a superior product of constant quality and utterly independent of the vicissitudes to which the natural oil is ever subjected.

The last shipments of the firm Sartorius in Manila have been distilled with the improved apparatuses recently sent from Europe and this distillate is of far superior quality to the former one obtained by means of the old appliances.

For less high requirements we can offer at a fair rate a second brand of oil, representing the customary prime quality of ylang-ylang oil.

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### Critical notes on recent papers concerning terpenes and essential oils.

Two papers of special interest to the theoretical study of terpenes have appeared since our last Report; the one by Mr. W. Euler<sup>1)</sup> treats of the constitution of isoprene, a hydrocarbon important by its close relations to the terpenes; the other by Prof. A. von Baeyer<sup>2)</sup> on the transformation of terpenes into benzol derivatives.

The constitution of isoprene, which upon condensation of two molecules, renders dipentene has recently been successfully elucidated by the researches of Ipatiew<sup>3)</sup> who has shown it to consist mainly of  $\beta$ -methyl divinyle and a small amount of trimethyl ethylene. He started his researches with isoprene from caoutchouc while Euler entered upon his inquiries by synthesis; reaching the same results as Ipatiew, he furnished valuable proofs to the observations made by this investigator. The material to start with was, in Eulers researches,  $\beta$ -methyl-*p*-dimethyl pyrrolidine, which when distilled with potassium hydroxide is broken up forming a base which by agglomeration of iodomethyl is converted into methyl-*p*-trimethyl pyrrolidyl ammonium iodide. By the action of potassium hydroxide, trimethylamine with the elimination of potassium iodide is formed, with the simultaneous formation of a hydrocarbon  $C_5H_8$ , which according to

<sup>1)</sup> Journ. f. prakt. Chem. (2) 57, 132.

<sup>2)</sup> Berichte der deutsch. chem. Ges. 31, 1401.

<sup>3)</sup> Journ. f. prakt. Chem. (2) 55, 4.

its origin should have the formula of a  $\beta$ -methyl divinyle  $\text{CH}_2 = \text{CH} - \text{C}(\text{CH}_3) = \text{CH}_2$ . This hydrocarbon has been found to be identical with the main constituent of the isoprene from caoutchouc, so that this may be considered beyond doubt as  $\beta$ -methyl divinyle.

Prof. von Baeyer has endeavored to study the benzol derivatives of the various terpenes. The mode of operation adopted by him has proved successful and he has converted the two monocyclical terpenes limonene and carvestrene into p- and m-cymol. His method has been applied to some other terpenes and the results are soon to be published. These studies are coupled with theoretical considerations whereby the transformation of carvone into the dihydrocarvone of the p-cymol series and that of carylamine into carvestrene of the m-cymol series are explained.

**Pinene.** Nitrosopinene,  $\text{C}_{10}\text{H}_{15}\text{NO}$ , originating from pinene-nitroschloride by elimination of hydrochloric acid, is converted by reduction into the base pinylamine,  $\text{C}_{10}\text{H}_{15}\text{NH}_2$ . This base can be converted by the action of nitrous acid into the alcohol pinocarveol,  $\text{C}_{10}\text{H}_{15}\text{OH}$ , and this again by oxidation into the ketone pinocarvone,  $\text{C}_{10}\text{H}_{14}\text{O}$ , isomeric with carvone. At the reduction of nitrosopinene not only pinylamine, but also a ketone  $\text{C}_{10}\text{H}_{16}\text{O}$ , isomeric with camphor and therefore called pinocamphone, is formed, which recently has been examined by Prof. Wallach.<sup>1)</sup> This ketone is, like camphor, a fully saturated compound, has a turpentine-like odor reminding one, when heated, of peppermint. When reduced, it is converted into the corresponding alcohol pinocampeol,  $\text{C}_{10}\text{H}_{17}\text{OH}$ , a viscous fluid of a terpeneol-like odor. Pinocamphone is distinguished by an oxime, melting at  $86^\circ$  to  $87^\circ$  and having an extraordinary tendency to crystallisation; it remains undecomposed when acted upon by dilute sulfuric acid, but by warm concentrated sulfuric acid it is converted mainly into a nitrile having an odor like campholene nitrile, which can be converted into an acid by heating it with alcoholic potassium hydroxide. Since the formation of pinocamphone by means of the reduction of nitrosopinene can be explained by supposing a process of hydrolytic dissociation with the simultaneous addition of hydrogen, the bromine addition product of nitrosopinene has likewise been submitted to the action of nascent hydrogen. The result was that neither pinylamine nor pinocamphone were formed but a ketone, isomeric with the latter compound and which has much in common with inactive dihydrocarvone; at the same time a base is formed quite different in its properties from pinylamine. Wallach is of the opinion that pinocamphone probably is the hydrocompound of the still unknown ketone corresponding to nitrosopinene.

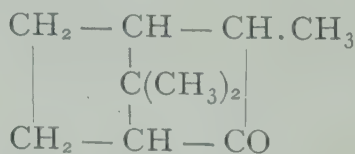
<sup>1)</sup> Liebig's Annalen 300, 286.

**Fenchene.** The disclosure of the constitution of fenchene by oxidation has been entered upon by Messrs. Gardner and Cockburn and by Prof. Wallach. The former two employ for oxidation the more active nitric acid, the latter prefers dilute permanganate solution, less prone to causing elementary dissociation.

Gardner and Cockburn<sup>1)</sup> submit fenchone upon a water bath to a mixture consisting of equal volumes of concentrated nitric acid and water; when the reaction, at first vehement, relapses, the acid mixture is added until the fenchene has disappeared. The volatile acids, particularly acetic acid formed by the reaction, are then removed by distillation and the remaining concentrated solution is allowed to stand for crystallisation a few days. The crystals are recrystallized, at first from strong nitric acid and subsequently from water; they melt at 207° and have proved upon examination to consist of camphopyric acid, C<sub>6</sub>H<sub>14</sub>O<sub>4</sub>. The fluid separated from the crystals yields, when distilled under reduced pressure, *cis*-camphopyric acid anhydride, melting at 178°.

Wallach<sup>2)</sup> by the oxidation of fenchene by means of potassium permanganate, obtained as the more important product of oxidation oxifenchenic acid, melting at 152° to 153°, marked by a relatively slightly soluble potassium salt; the formula of the acid is C<sub>10</sub>H<sub>16</sub>O<sub>3</sub> and its properties correspond to those of *α*-oxiacids. When it is acted upon by oxidizers, carbonic acid is eliminated and fenchocamphorone, C<sub>9</sub>H<sub>14</sub>O, a ketone isomeric with phorone is obtained, this melts at 109° to 110° and is a true lower homologue of camphor and very similar to this. Fenchocamphorone has the character of a saturated bicyclic ketone; by the addition of hydrogen, it forms the corresponding alcohol fenchocamphorol, C<sub>9</sub>H<sub>16</sub>O, melting at 128° to 130°. It forms with hydroxylamine an oxime, melting at 69° to 70°; which, like camphoroxime, is converted into an oily nitrile of an odor similar to that of campholennitrile, when heated with dilute sulfuric acid. Dilute nitric acid oxidizes fenchocamphorone, converting it into a mixture of two acids, the one melting at 124°, the other at 202°; the latter is the richer one in carbon, has the formula C<sub>9</sub>H<sub>14</sub>O and possibly is identical with the camphopyric acid of Gardner and Cockburn<sup>3)</sup>.

When the formula of fenchone is accepted to be

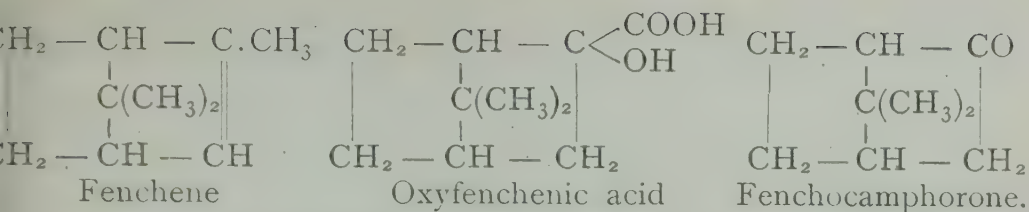


those of the other compounds may be deduced to be:—

<sup>1)</sup> Journ. of the chem. soc. 73, 275.

<sup>2)</sup> Liebig's Annalen 300, 313.

<sup>3)</sup> Journ. of the chem. soc. 69, 74.



In our laboratory too fenchene has been submitted to a close investigation. Since it is not unlikely that it is contained in some essential oils, we aimed to obtain solid derivatives in order to acquire thereby a means for its identification. We failed, however, to obtain such products of addition, but we ascertained that fenchene, like camphene which furnishes isoborneol, when acted upon by acetic and sulfuric acid, renders by hydration a compound  $\text{C}_{10}\text{H}_{18}\text{O}$ , melting at  $61.5^\circ$  to  $62^\circ$ , isomeric with fenchylalcohol. This isoborneol, however, does not yield the well known fenchone, when acted upon by oxidizers, but an isomer rendering an oxime melting at  $82^\circ$ . An explicit paper on these compounds will soon be published in the "Journal für praktische Chemie".

**Menthol and its compounds.** The number of known menthols has been increased by one. Its origination shows it to have the same structure as the natural l-menthol; from this it differs, however, considerably by its properties. By the reduction of the 3-methyl-6-isopropyl- $\Delta^2$ -keto-R-hexene Mr. S. H. Baer<sup>1)</sup> has obtained an alcohol  $\text{C}_{10}\text{H}_{20}\text{O}$  which forms an oily liquid; its odor is sweetish faintly recalling that of peppermint, it boils at  $202^\circ$  to  $204^\circ$ , has the specific gravity of 0.910 at  $20^\circ$  and forms no urethane when acted upon by phenyl-isocyanate. By the elimination of the elements of water by means of phosphoric anhydride, this synthetic menthol is converted into an inactive menthene, forming an oily liquid of a benzole-like odor and boiling at  $165^\circ$  to  $167^\circ$ . It forms an unstable dibromide, a somewhat more stable monobromide, but no nitrosyle compound. In these properties this inactive menthene differs from the ordinary menthene formed from l-menthol by the elimination of the elements of water.

Professor Wallach<sup>2)</sup> has made the observation that the two (l- and d-) menthylamines originating upon the decomposition of l-menthone when acted upon by ammonium formiate, show a different reaction with nitrous acid; l-menthylamine yields the ordinary l-menthone while d-menthylamine yields very little menthol and probably some menthone but mainly a hydrocarbon  $\text{C}_{10}\text{H}_{18}$ . This indicates that d-menthol, standing in relation to d-menthylamine, is more inclined to the elimination of the elements of water than the

<sup>1)</sup> Inaugur. Dissertation. Leipzig 1898.

<sup>2)</sup> Liebigs Annalen 300, 278.

ordinary menthol. It furthermore indicates that the hydroxylgroup of d-menthol must stand in closer structural relation to the tertiary hydrogenatom linked to the adjoining carbonatom than is the case with l-menthol. The isomery of the two menthylamines, therefore, rests upon cis-trans-isomery. Menthene, formed from d-menthylamine by the action of nitrous acid, boils at  $164^{\circ}$  to  $165^{\circ}$ , has the specific gravity of 0.8175 and renders a nitrosochloride which can be converted by the action of benzylamine into a nitrolamine melting at  $107^{\circ}$  to  $108^{\circ}$ . Both menthylamines can be converted into menthene in the same way by converting them into the corresponding menthyl-trimethyl-ammoniumiodides by means of consecutive action with iodomethyl. The iodides are deprived of their iodine by treating them with moist oxide of silver and the remaining ammonium bases are submitted to dry distillation; l-menthyl-trimethyl-ammonium-hydroxide, after the elimination of the elements of water and some trimethylamine, yields menthene  $C_{10}H_{18}$ , boiling at  $170^{\circ}$  to  $171^{\circ}$ ,  $d_{18^{\circ}}$  0.811;  $(\alpha)_D = +89^{\circ}30'$ , while the corresponding dextrocompound is converted into a hydrocarbon, boiling at  $107^{\circ}$ . This only forms a nitrosochloride, melting at  $116^{\circ}$  to  $118^{\circ}$ .

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Mr. Konowalow<sup>1)</sup> has continued his previous studies of the nitrogen compounds of the menthol series. When concentrated nitric acid of the specific gravity of 1.075 is allowed to act upon menthone at a temperature of  $80^{\circ}$  and under constant stirring, nitro-menthone results; this forms a heavy ( $d_{20^{\circ}} = 1.059$ ) liquid and is converted into amido menthone when reduced by the action of tin and hydrochloric acid. It forms a limpid, colorless fluid, soluble in water, and boiling at  $235^{\circ}$  to  $237^{\circ}$  under ordinary pressure and almost without any decomposition. Of its derivatives the oxime is remarkable; its hydrochloride, melting at  $110^{\circ}$ , is obtained when free amidomenthone is allowed to act upon an excess of hydroxylamine-hydrochloride. Amidomenthonoxime is converted by reduction into a liquid diamine boiling at  $240^{\circ}$  to  $243^{\circ}$ ; the hydrochloride of this reacts vehemently with potassium nitrite forming a neutral compound of a menthol-like odor. This may possibly be an unsaturated ketone identical or isomeric with pulegone. When acted upon by reducing agents, amidomenthone combines with two hydrogen atoms, forming amidomenthol, a glycerin-like liquid which boils at  $254^{\circ}$  under ordinary pressure.

The investigation is to be continued.

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<sup>1)</sup> Berichte der deutsch. chem. Ges. 31, 1478.

When Bourbon-geranium oil is saponified and then acted upon by phthalic acid anhydride in order to fix geraniol and citronellol, according to Flatau and Labbé<sup>1)</sup> about 15 per cent of indifferent matter remains behind; half of this distills between 105°—110° at 15 Mm. pressure. This fraction has a pleasant peppermint-like odor and has been examined for menthone; the authors succeeded by repeated fractionation to separate a substance boiling at 204° to 206°, which rendered a semicarbazone, melting at 179.5°, when acted upon by semicarbazide hydrochloride. This semicarbazone was found to be identical with the corresponding compound obtained from ordinary menthone. Although the authors by their researches have proved the identity of menthone from Bourbon-geranium oil and common l-menthone, they nevertheless designate the former as  $\alpha$ -menthone. This useless designation can only bring about confusion. It may also be added that the semicarbazone described by Messrs. Flatau and Labbé had previously been known to Prof. Wallach<sup>2)</sup>.

**Borneol and its compounds.** Ordinary l-menthonoxime is converted into a symmetrical menthylamine when reduced by the action of sodium and alcohol, having an optical rotation corresponding to that of l-menthonoxime. The contrary is the case with the oxime of the ordinary d-camphor, Forster<sup>3)</sup>. Obtained, by reduction with sodium and amylic alcohol, a bornylamine which has a higher melting point than heretofore stated. He has succeeded in decomposing the product of the reaction into two bases, bornylamine and neobornylamine, differing by their melting points, 163° and 180°, as well as by their optical properties, the former having the optical rotation of +45.5°, the latter one of -31.3°. The dextrogyre base amounts to 60 per cent, the lævogyre one to 40 per cent. A number of derivatives prepared from both bases show also perceptible differences. For these details reference must be had to the original paper. It would be of interest to ascertain whether both bases will render a reaction with nitrous acid similar to that of the various menthylamines.

The amidomenthone of Konowalow and Ischewsky is converted into amidomenthol by reducing agents. In the same way the amidocamphor, originating from isonitrocamphor when acted upon with zinkdust, is converted into amidoborneol by the addition of hydrogen<sup>4)</sup>. While amidomenthol is a liquid, amidoborneol is obtained by crystallization from ether saturated with water in thick crystals containing water of crystallization, and from ligroïne in thin

<sup>1)</sup> Bull. soc. chim. Paris (3) 19, 788.

<sup>2)</sup> Ber. d. deutsch. chem. Ges. 28, 1955.

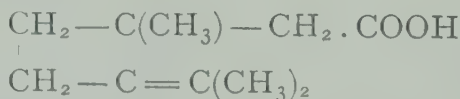
<sup>3)</sup> Journ. chem. soc. 73, 386.

<sup>4)</sup> Duden and McIntyre in Ber. d. deutsch. chem. Ges. 31, 1902.

scales. After having been dehydrated at 90° the anhydrous base melts at 187°, has a peculiar, penetrating odor and can readily be sublimed. Its hydrochlorate renders when acted upon by potassium-cyanate in aqueous solution, an urea melting at 177°, which may well serve for characterizing the original base.

**Pulegone.** Prof. Wallach<sup>1)</sup> reports on the synthesis of a pulegone which is very similar to the natural one. The main points of his paper have been noted on p. 57 of our Report of April 1897. Prof. Wallach has now published in an additional paper<sup>2)</sup> the results of his further researches on pulegenic acid formed from pulegone bibromide by disengagement of hydrobromic acid. Pulegenic acid is converted into a lactone  $C_{10}H_{16}O_2$ , when the hydrochlor-pulegenic acid methylester formed by the esterification of pulegenic acid by chlorhydric addition is acted upon by sodium methylate at a high temperature. Saponification and dissociation of hydrogen chloride take place at the same time, but the product of the reaction is not homogeneous; it contains, besides the lactone just mentioned and boiling at 125° to 127° (15 Mm. pressure), an acid, by its boiling point (256° to 260°) and specific gravity (0.9055) nearly conform with pulegenic acid, they are, however, isomeric, for the amide obtained therefrom does not melt like that of pulegenic acid at 121°, but at 152°. Remarkable is the reaction of pulegenic acid with alkaline hypobromites, the former being converted thereby into a brominated lactone, which when acted upon by sodium methylate, dissociates hydrogen bromide and a saturated lactone, pulegenolide  $C_{10}H_{14}O_2$ , melting at 44° to 45° and boiling at 265° to 368°. When it is boiled with an alkali the corresponding oxilactone  $C_{10}H_{10}O_3$ , melting at 95°, is formed. Pulegenolide and oxilactone,  $C_{10}H_{16}O_3$ , melting at 129°, formed by direct oxidation of pulegenic acid and already previously described by Prof. Wallach, stand in some relation to each other; for the lactone  $C_{10}H_{14}O_2$  can finally be obtained from the oxilactone by the substitution of the hydroxylgroup by chlorine and by subsequent elimination of hydrogen chloride. On the other hand, the conversion of the brominated lactone into the oxilactone  $C_{10}H_{16}O_3$  is not readily accomplished.

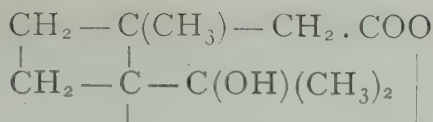
When the formula



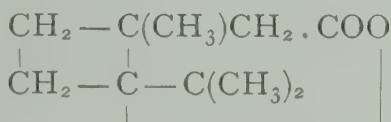
is attributed to pulegenic acid, these formulas can be deduced, for the oxilactone

<sup>1)</sup> Liebig's Annalen 300, 267.

<sup>2)</sup> Liebig's Annalen 300, 250.

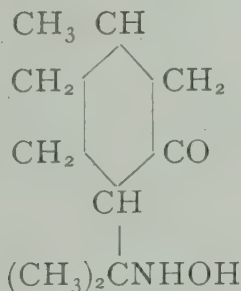


and for pulegenolide

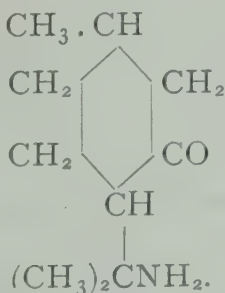


Three oximes of natural pulegone are known to exist, two of these have a normal constitution and are isomeric, whilst the third discovered by Messrs. Beckmann and Pleissner contains, in addition, the elements of water and therefore has been named pulegon-oxime hydrate.

From the observations with mesityloxyde made by Messrs. Harries and Jablonsky, Harries and Roeder<sup>1)</sup> suppose that the action of hydroxylamine upon pulegone takes place in the same way, namely that it is not the ketone group that reacts with the hydroxylamine, but that an addition to the double linkages takes place. Accordingly pulegonoximehydrate has the formula of a pulegonehydroxylamine:—



corresponding to this, the oximehydrate renders upon oxidation a true nitroso compound, nitrosomenthone, melting at 35°. This also explains the observation made by Messrs. Beckmann and Pleissner, that pulegonoximehydrate forms an oxygenated base when acted upon by reducing agents, this is the 8-aminomenthone



<sup>1)</sup> Ber. d. deutsch. chem. Ges. 31, 1809.

**Aliphatic compounds of the terpene series.** Prof. F. Tiemann has recently published a paper under the title "On violet ketones and the related compounds of the citral- (geranial-) series"<sup>1)</sup>, containing a compilation of recent investigations in this domain and some additional new observations. The paper is preceeded by a comprehensive consideration of the constitution of irone and ionone, determined by synthesis and by decomposition of the respective compounds, and contains an essay on the individual members of the citral series.

For the characterisation of citral, Prof. Tiemann recommends its transformation into citryl- $\beta$ -naphthocinchonic acid melting at  $197^{\circ}$ , discovered by Döbner. The reaction of citral with semicarbazide is unavailing for detecting the presence of this aldehyde because, as already shown by Wallach, a mixture of semicarbazons is formed which melts between  $130^{\circ}$  to  $140^{\circ}$ .

Furtheron Prof. Tiemann describes the synthesis of geranic acid and isogeranic acid found by Barbier and Bouveault while allowing iodo- or bromo-acetic ester and zink to act upon methylheptenone.

By the dry distillation of calcium geraniate and formiate, citral was obtained; therefore citral also belongs to the series of organic compounds whose synthetic preparation has been secured.

Prof. Tiemann rejects the proposition made to replace the name geraniol for the alcohol  $C_{10}H_{18}O$  by that of rhodinol, deeming it more proper altogether to discard the superfluous name of rhodinol, since its continuation can only lead to confusion.

Upon the action of hydrochloric acid upon geraniol a mixture of isomeric chlorides  $C_{10}H_{17}Cl$  is formed, which gave rise to alcohols  $C_{10}H_{18}O$ , when acted upon by alcoholic potassa; they were found to contain, besides regenerated geraniol, about 50 per cent of inactive linalool.

Prof. Tiemann recommends the following method of the preparation of pure linalool from essential oils: To the crude linalool contained in a retort, sodium in pieces is added, the air is removed as near as possible from the retort and this is heated as long as sodium is being dissolved. After cooling, the liquid is separated from the undissolved sodium, some ether and then gradually as much phthalic acid anhydride is added as is equivalent to the amount of sodium dissolved. After two days standing water and alkali are added, whereby the linalylphthalicester acid is dissolved, while the excess of linalool and linaloolene remains dissolved in the ether. The sodium salt of the linalylphthalicester acid is purified by shaking it with ether and is treated with alcoholic potassa, whereby pure linalool is set free.

<sup>1)</sup> Berichte d. deutsch. chem. Ges. 31, 808.

Pseudoionone,  $C_{13}H_{20}O$ , obtained by the condensation of citral and acetone is best purified by boiling the crude product with a solution of sodium bisulfite; the pseudoionone is hereby dissolved, the solution is purified by shaking it with ether and the pseudoionone is subsequently set free by the addition of a solution of sodium hydrate. When sulfuric acid is used in place of sodium, part of the pseudoionone is inverted into ionone.

When acted upon by semicarbazide, pseudoionone behaves similar as does citral, in not yielding a homogenous product but a mixture of semicarbazones melting at  $110^{\circ}$  to  $142^{\circ}$ . When treated with *p*-bromphenylhydrazine, pseudoionone is converted into a readily decomposed bromphenylhydrazone melting at  $102^{\circ}$  to  $104^{\circ}$ .

The detection of pseudoionone is best accomplished by converting it by the action of dilute acids into cyclical ionone, and by identifying this by means of the ionone-*p*-bromphenylhydrazone, melting at  $142^{\circ}$  to  $143^{\circ}$ . When the inversion of pseudoionone is made by means of the action of concentrated sulfuric acid,  $\beta$ -ionone, to be considered later on, is mainly formed; this gives a semicarbazone melting at  $148^{\circ}$ .

Ionone is purified by boiling it with a sodium bisulfite solution in the same way as is described with pseudoionone.

For the detection of ionone, the *p*-bromphenylhydrazone, melting at  $142^{\circ}$  to  $143^{\circ}$  is best applied.

In conclusion Prof. Tiemann dwells upon the systematic decomposition of ionone by means of oxidation with potassium permanganate; hereby oxionolactone,  $C_{10}H_{16}O_3$ , geronic acid,  $C_9H_{16}O_3$ , as- $\beta$ -dimethyladipinic acid, as- $\alpha$ -dimethylglutaric acid and as-dimethylsuccinic acid are formed.

In an additional paper<sup>1)</sup> Prof. Tiemann dwells upon the decomposition of ionone into  $\alpha$ - and  $\beta$ -ionone. When pseudoionone is inverted by the action of concentrated sulfuric acid, an ionone is formed which differs from ordinary ionone by rendering a semicarbazone melting at  $148^{\circ}$ , while the semicarbazone of ordinary ionone melts at  $109^{\circ}$  to  $110^{\circ}$ . From this semicarbazone the new ketone, called  $\beta$ -ionone, can be separated by the action of sulfuric acid. When it is treated again with semicarbazide, semicarbazone melting at  $148^{\circ}$  is restored.

*p*-bromphenylhydrazone of  $\beta$ -ionone melts at  $115^{\circ}$  to  $116^{\circ}$ , while  $\alpha$ -ionone-*p*-bromphenylhydrazone melts at  $142^{\circ}$  to  $143^{\circ}$ .

Ordinary ionone is also converted into  $\beta$ -ionone when acted upon by concentrated sulfuric acid.

It has finally been shown that all ionone preparations contain, besides  $\alpha$ -ionone, more or less considerable admixtures of  $\beta$ -ionone.

<sup>1)</sup> Berichte d. deutsch. chem. Ges. 31, 867.

In order to separate both ketones, a solution of the ordinary ionone-semicarbazone in ether or ligroine is cooled down to a rather low temperature, whereby most of the  $\beta$ -ionone semicarbazone separates in crystals. From the semicarbazone remaining in the mother liquor, the ionone is set free and converted into the oxime. From this solution  $\alpha$ -iononoxime, melting at  $89^\circ$  to  $90^\circ$  is obtained in crystals when the liquid is exposed to a freezing mixture.  $\alpha$ -iononoxime renders pure  $\alpha$ -ionone when acted upon by sulfuric acid.

Both ionones have much similarity, the boiling point of the  $\beta$ -modification is by some degrees higher than that of  $\alpha$ -ionone. The oxime of  $\alpha$ -ionone melts, as stated above, at  $89^\circ$  to  $90^\circ$ , while that of  $\beta$ -ionone remains viscid. The differences between the semicarbazones and p-bromphenylhydrazones have been referred to on page 55.

When oxidized by the action of potassium permanganate, both ionones render the same decomposition products, namely oxionolactone, geronic acid etc. By the action of hydroiodic acid both ionones are reduced to the same hydrocarbon,  $C_{13}H_{18}$  (ionene), which by oxidation is converted into ioniregentricarbonic acid,  $C_{12}H_{12}O_6$ .

In connection with these publications of Prof. Tiemann, Mr. J. Ziegler<sup>1)</sup> calls attention to some differences existing between ionone and the violet-oil preparations prepared by him by the condensation, by means of acetone, of the parts of lemon-grass oil with a higher boiling point.

"Pseudoviolet oil" renders a semicarbazone melting at  $143^\circ$ , while Tiemann's pseudoiononesemicarbazone melts at  $110^\circ$  to  $142^\circ$ .

From the "violet oil" obtained from "pseudoviolet oil" by inversion by means of acid sodium sulfate, Ziegler succeeded in obtaining a semicarbazone melting at  $142^\circ$  and a p-bromphenylhydrazone melting at  $146^\circ$ .

Tiemann found  $\alpha$ -iononesemicarbazone to melt at  $107^\circ$  to  $108^\circ$ ,  $\beta$ -iononesemicarbazone at  $148^\circ$ ,  $\alpha$ -ionone-p-bromphenylhydrazone at  $142^\circ$  to  $143^\circ$  and the  $\beta$ -compound at  $115^\circ$  to  $116^\circ$ .

Ziegler is of the opinion that the "violet oil", prepared by him is not derived from geranial, but from other as yet unknown aldehydes contained in lemongrass oil.

Döbner<sup>2)</sup> has taken up the same problem. By the action of pyrrolic acid and naphthylamine upon citral and lemongrass oil, and by the subsequent determination of the weight of the citryl- $\beta$ -naphthocinchonic acid, he ascertained the amount of citral contained in lemongrass oil to be 82 per cent. At the same time he

1) Journ. f. prakt. Chem. N.F. 57, 493.

2) Berichte d. deutsch. chem. Ges. 31, 1888.

showed that besides the citral no considerable amount of other aldehydes is contained in the oil.

It was furthermore ascertained that "pseudoviolet oil", obtained by the action of chlorinated lime and cobalt nitrate upon lemongrass oil and acetone in alcoholic solution, is identical with Tiemann's pseudoionone, as also that "violet oil", obtained from "pseudoviolet oil" by inversion with acid sodium sulfate, is in all essential points also identical with ionone.

Another paper on this subject by Mr. W. Stiehl "Contributions to our knowledge of lemongrass oil"<sup>1)</sup> shows him to have reached quite different results.

According to Mr. Stiehl, lemongrass oil contains at least three different aldehydes  $C_{10}H_{16}O$ ; they are

1. Citral (geranial),
2. Citriodoraldehyde<sup>2)</sup>,
3. Allo-lemonal.

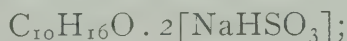
They differ in their action on sodium bisulfite solution. They render at common temperature normal bisulfite compounds



little soluble; they show, however, upon warming the liquid containing them in suspension, quite a different behavior.

The crystalline sodium bisulfite salt of citral (geranial) is thereby converted into the readily soluble sodium salt of a true sulfonic acid, from which the aldehyde is not regenerated either by sodium hydroxide or by sodium carbonate.

The solid sodium bisulfite salt of citriodoraldehyde is also converted upon heating into a readily soluble sodium salt,



but this differs from the corresponding salt of citral in its being decomposed by the action of sodium hydroxide with the disengagement of the citriodoraldehyde.

The sodium bisulfite salt of allolemonal is an unstable compound, decomposing into its component parts, allomenal and sodium bisulfite, when warmed.

This difference in the properties of the sodium bisulfite compounds of aldehydes has been made use of by Mr. Stiehl for their separation and isolation. For a comparison of the three aldehydes, Mr. Stiehl prepared their semicarbazones, their  $\beta$ -naphthocinchonic acids, their aceton condensation products (pseudoionones) and their semicarbazones. The result is made plain by the following table:—

<sup>1)</sup> Journ. f. prakt. Chem. 58, 51.

<sup>2)</sup> See Dodge, Am. Chem. Journ. 12, 553 to 564.

	Citriodor- aldehyde	Citral (geranial)	Allolemonal
Boil. p. under 12 Mm. pressure	108° to 109°	111° to 112°	117.5° to 119°
" " " 760 " "	228° to 229°	225° to 227°	233° to 235°
Specific gravity at 20° . .	0.8883	0.8868	0.9017
Refraction exponent $n_D$ 20°	1.48538	1.48752	1.48306
Optical rotation (100 Mm. $\alpha_D$ )	$\pm 0^\circ$	$\pm 0^\circ$	$-5^\circ 5'$
Semicarbazone, melting point	134° <sup>1)</sup>	141° <sup>1)</sup>	169°
$\beta$ -naphthocinchoninic acid, melting point. : . . .	204°	197°	235°
Aceton condensation product			
$C_{13}H_{20}O$ , boiling point .	149° to 152°	143° to 145°	157° to 159°
ditto, specific gravity at 20°	0.8980	0.9037	0.9000
" refraction exponent .	1.52903	1.52738	1.53150
" semicarbazone, melt- ing point . . . .	134° to 135°	110° to 112°	142° to 143°

From this table it becomes evident that citriodor-aldehyde and citral are very similar, the only considerable differences being the melting points, 204° and 197° for the two  $\beta$ -naphthocinchoninic acids, and 134° to 135° and 110° to 112° for the semicarbazones of the aceton condensation products. These, however, are not quite unobjectionable because both, pseudoionone and citral, as ascertained by Prof. Tiemann, do not form a homogenous semicarbazone.

Allolemonal, however, differs much from the other aldehydes by its optical reaction, by its higher boiling point, by the melting point of the naphthocinchoninic acid &c.

According to Mr. Stiehl's observation, the three aldehydes seem to be capable of being readily converted one into the other. This takes place particularly under the influence of dilute acids, even by the action of a bisulfite solution. Citriodor-aldehyde is said readily to be transformed into geranial. On the other hand, geranial can be converted into the other aldehydes by boiling it with sodium acetate solution.

Lemongrass oil contains, according to Mr. Stiehl, about

10 per cent of citral (geranial),  
40 to 50 " " " citriodor-aldehyde,  
25 " 30 " " " allolemonal.

Small quantities of terpenes, of dipentene and of limonene (?), were also found, but no methylheptenone nor geraniol.

A conclusive estimate of the paper of Mr. Stiehl can not be made without a careful repetition of his examinations. A few reflections on his conclusions, however, may already now be advanced.

1) Mixtures whose melting points are modified by recrystallisation.

As long ago as in 1888, we called attention to the presence of an aldehyde  $C_{10}H_{16}O$  in lemongrass oil, in lemon oil and in certain eucalyptus oils; we called this aldehyde citral and brought it into commerce under this name soon afterwards. From the start we have prepared this product from lemongrass oil by means of its sodium bisulfite compound, which is readily soluble in water and can easily be decomposed by alkaline hydroxides. This is the simplest and easiest manner of its preparation. Our "citral", therefore, is identical with Mr. Stiehl's "citriodor-aldehyde". Meanwhile, Professor Semmler by comparing his geranial obtained by the oxidation of geraniol with our "citral" (Stiehl's "citriodor-aldehyde"), succeeded in ascertaining the identity of the two, as was corroborated later on by Mr. Döbner, who also used our "citral" for comparison.

According to our experience, our "citral" (Stiehl's citriodor-aldehyde) is completely converted into the true sulfonic acid compound when properly acted upon by sodium bisulfite. This sulfo-compound withstands the action of alkalies.

On the other hand, the dissociation of aldehyde will always have to take place when heated with sodium bisulfite compounds as long as the quantity of sodium bisulfite present is insufficient for forming the compound  $C_{10}H_{16}O + 2(NaHSO_3)$ , which always is the case in Mr. Stiehl's experiments. For this reason Mr. Stiehl's method of the separation of "allolemonal" is not unobjectionable.

Commercial "citral", obtained by the above mentioned method, is always optically inactive, but never has a constant boiling point, notwithstanding the careful purification of the sodium bisulfite compound. We have so far been of the opinion that the reason for this consisted in the oxidation or polymerisation of the readily decomposing compound, but are now about to find out whether this behavior of the preparation may be due to the presence of various aldehydes.

Contrary to the statements made by Stiehl we have found methylheptenone and geraniol to be permanent constituents of the lemongrass oil. We have isolated both repeatedly from the oil not yet treated with bisulfite and identified them with utmost security.

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Messrs. Flatau and Labbé<sup>1)</sup> have published a process for the separation of geraniol and citronellol. The respective essential oil is at first saponified and subsequently distilled in a vacuum. The fraction obtained between  $120^{\circ}$  to  $140^{\circ}$  under 30 Mm. pressure is boiled for one hour in a reflux condenser with an equal weight of phthalic acid anhydride and an equal volume of benzol. Then soda is added, and the whole dissolved in water; this solution is shaken

<sup>1)</sup> Compt. rend. 126, 1725. — Bull. soc. chim. III, ser. 19, 633 ff.

out with ether and finally acidulated with hydrochloric acid. In this way the acid phthalicester of geraniol and citronellol is set free. These esters are dissolved in ligroine and the solution cooled down to  $-5^{\circ}$ . In doing so geranylphthalicester acid is said to quantitatively separate in crystals, while citronellylphthalicester acid remains in solution. By decomposition of the acid esters by means of alcoholic potassa, the free alcohols are obtained which are purified by rectification.

We have submitted this method to a practical test and have found it well suited for the preparation of pure geraniol. The separation of the crystals readily takes place and the alcohol obtained therefrom is just as pure as that obtained by the calcium-chloride method. But we have not succeeded in this way to get pure citronellol; the products always contained variable quantities of geraniol as is easily to be seen from their reaction with calcium-chloride. The reason is that geranylphthalicester acid at  $-5^{\circ}$  is not quite insoluble in ligroine. For this reason this method is unfit for the quantitative determination of the two alcohols in essential oils and the figures published by Mrs. Flatau and Labbé require discrimination. They for instance state palmarosa oil (Indian palmarosa oil) to contain 63 per cent of geraniol and 17 per cent of citronellol. The fact is that of the latter alcohol only traces are contained in the oil or none at all.

The melting point of geranylphthalicester acid is at  $48^{\circ}$ , that of its silversalt at  $133.8^{\circ}$ . Tetrabromgeranylphthalicester acid, obtained by the action of bromine upon a cold ethereal solution of geranylphthalicester acid, melts at  $114^{\circ}$  to  $115^{\circ}$ . All these three compounds may be used for characterizing geraniol.

By heating geraniol with alcoholic potassium hydroxide for some time, Mr. Barbier<sup>1)</sup> obtained a new tertiary alcohol, boiling at  $79^{\circ}$  under 10 Mm. pressure, whose odor recalls that of methylheptenone. According to Mr. Barbier, the alcohol has the composition  $C_9H_{18}O$  and may be considered a dimethylheptenol. When oxidized by means of chromic acid, acetone, methylheptenone and lævolinic acid are formed. When acted upon by dilute sulfuric acid, some stable glycol is at first formed, and subsequently by the elimination of the elements of water, dimethylheptenoxide, a liquid boiling at  $132^{\circ}$  to  $133^{\circ}$  and having a peppermint-like odor.

According to Mr. Barbier, linaloe oil also contains dimethylheptenol; this he concludes from his having obtained in the preparation of the so-called "licarhodol" portions with a low boiling point ( $83^{\circ}$  to  $85^{\circ}$  under 10 Mm. pressure) which had the odor of dimethylheptenol acetate.

<sup>1)</sup> Compt. rend. 126, 1423.

Being much interested in this subject, we have repeated the experiments of the French scholar, and can only confirm his statements. By the analytical results and in the main comparative investigation, however, we are inclined to the opinion that the alcohol is not dimethylheptenol  $C_9H_{18}O$  but methylheptenol  $C_8H_{16}O$ , whose formation from geraniol is readily explained. Nor do we believe that methylheptenol or dimethylheptenol are contained in linaloe oil to any extent. The alcohol observed in the preparation of "licarhodol" having so low a boiling point is in our opinion a product of decomposition of linalool.

After the conclusion of our researches we may once more have to return to this subject.

We referred in the April number of our Report of the present year to an investigation about the "licarhodol" of Mr. Barbier. It furnished the evidence that licarhodol consists of a mixture of about 15 parts of terpeneol and 85 parts of geraniol and that it can by no means be considered to be a distinct chemical substance. We then could not isolate the terpeneol in a solid form. This investigation has been continued and the results have recently been published in a paper "Ueber eine Umwandlung von Linalool in Terpeneol vom Schmelzpunkt  $35^{\circ}$ "<sup>1)</sup>. The main results may here briefly be stated.

Acetic acid anhydride acts upon l-linalool, forming a dextro-gyre acetate; this is, after having been saponified, Barbier's<sup>2)</sup> licarhodol. This yields upon repeated fractionation under decreased pressure a fraction which solidifies in a freezing mixture, and after repeated recrystallisation from its solution in petroleum ether shows all properties of terpeneol. Its melting point is  $33^{\circ}$  to  $35^{\circ}$ , sp. gr. 0.936 at  $15^{\circ}$ ;  $[\alpha_D]$  at  $20^{\circ} = +16^{\circ}12'$ , its boiling point  $216^{\circ}$  to  $218^{\circ}$  under 10 Mm. pressure. When treated with carbanil terpenylphenylurethane melting at  $112^{\circ}$  to  $113^{\circ}$  was obtained. Licarhodol, therefore, contains, besides geraniol, also d-terpeneol.

In the same way but much more easily, l-linalool can be transformed into d-terpeneol by the action of formic acid and of acetic and sulfuric acid, care being taken that the temperature does not rise beyond  $+20^{\circ}$  during the action of these reagents. The yield amounts to about 50 per cent of the linalool used.

Coriandrol, the optical antipode of l-linalool, when treated in the same way, is converted into l-terpeneol.

<sup>1)</sup> Journ. f. pract. Chem., N. F., 58, 109.

<sup>2)</sup> Compt. rend. 116, 1200.

**Citronellol, pure.** This excellent product, first brought into commerce in a pure condition by us, has more and more met with the appreciation of experts. We have in consequence been induced to manufacture the same on a large scale. The only drawback to its general application consists in its high price.

**Cumarin.** Cutting of prices has continued without consideration of the troublesome process of the manufacture of the article. Since 1880 the price has gradually declined from *ℳ* 400.— to *ℳ* 50.— per kilo, while the use of cumarin has constantly and most extensively increased. All the price cutting has been to the advantage and profit of the perfumery- and soap industries.

**Eucalyptol (Cineol).** The consumption of this article is a steady one and has much increased since the time when a pure crystallized product can be furnished at fair rates. This would increase still more if the product should be recognized by the pending new edition of the German pharmacopœia. The new British pharmacopœia has failed to do this.

**Heliotropine.** The price of this commodity has suffered a further reduction by *ℳ* 2.— per kilo during the last six months. This seems to unsettle some manufacturers. We started the manufacture of heliotropin in 1881, supplying the market with the first lot of our product on Juli 1<sup>st</sup> at the price of *ℳ* 10.50 per kilo. The reduction from this rate to *ℳ* 30.— per kilo may be unprecedented in chemical industry.

**Ionone.** The price of the original product of Messrs. Haarmann & Reimer in Holzminden, has remained unaltered. On account of its uniform and pure qualities their product continues to meet with general appreciation.

Messrs. Haarmann & Reimer request us to mention here that they will, in sometime, offer to the trade a new product under the name of Sapirone. It is not a substitute for ionone, the less so as it is devoid of the fragrance of fresh violets, but it is said to be an excellent adjunct for fixing the violet odor in toilet soaps. Sapirone is a fluid similar to essential oils.

**Menthol, crystallized.** What has been said about Japanese oil of peppermint on p. 36 of this Report also holds good for the raw material serving for the preparation of menthol crystals. A further reduction of prices is not possible except for unforeseen discreditable practices or transactions.

Since our last Report the following communications about the use of menthol crystals have appeared.

Mr. Jousset<sup>1)</sup> recommends menthol inhalations as an efficient remedy against acute frontal head achè. One coffeespoonfull of a

<sup>1)</sup> Sem. méd. 1898.

solution of 5 Gm. of menthol and 2 Gm. of rectified oil of turpentine in 100 Gm. of alcohol is poured into a cupfull of hot water and the vapors are drawn up by the nose for several minutes. This is to be repeated once every hour.

Dr. M. Saenger in Magdeburg<sup>1)</sup> also prefers in the treatment of acute cold in the head a 10 percent menthol solution, which gives immediate relief. He adds that menthol vapors act just as well as cocain in congestions of the mucus membranes of the nose and of head-ache resulting therefrom, without the untoward after-effects of cocaine.

Menthol has been recognized by the new British Pharmacopœia, not however the pure crystals, but the crude impure ones, "usually more or less moist from adhering oil", as is said verbally in this work.

The menthol of the German pharmacopœia, on the other hand, is the pure product, for which a "brittle" structure of the crystals and the melting point of 43° are required.

**Safrol.** The prices of the raw material still range high and show considerable variations in its quality so that due discrimination has to be exercised in purchases. A further decline of prices is not possible.

**Terpineol.** The demand for this article was regular and prices remained unaltered. In connection with it we cannot but call attention to the following ordinance of the Italian custom-house authorities, issued August 3<sup>rd</sup> 1897:—

No. 67. Terpine a pharmaceutical product, for the manufacture of which alcohol is required, is subjected, besides the entrance duty of 10 liras per 1 dz (T. No. 69), to the additional alcohol manufacturing tax in the proportion of 2 liters to each kilo net of the product. The fact that by treaties with Germany and Austro-Hungary the import duty of terpine is fixed at 10 lire can not come into consideration, since the requirements of the tariff and of the whiskey tax were already in force at the time these treaties were made; these requirements refer to imported medicinal articles, which, besides the import duty, must pay the tax for the alcohol either contained therein or used in their manufacture. (Ordinance of August 3<sup>rd</sup> 1897.)

**Thymol, crystallized.** In consequence of unfavorable chances in the markets of the raw material, ajowan seeds, the rates of this article had to be raised considerably some months ago. The traffic in the Northern Provinces of India seems to have been completely disorganized by the pestilence prevailing there since some time; a regular supply of products, among them also ajowan-seeds, has in consequence been checked. Besides, the consumption of the seeds in the districts of their production may require the greater part of it, since the antiseptic properties of the seeds were well known in India a long time before the manufacture of thymol in Europe commenced. The principal market of the seed is Marevar in the Pro-

<sup>1)</sup> Therap. Monatshefte XII, 383.

vince of Rajputana. The crystals (*Ajovín-kaphúl*) come from Oojein<sup>1</sup>). For this product the melting point in the new British Pharmacopœia, lying between 43.3° to 51.7° C. is too liberally given. Pure Thymol should not melt at a lower temperature than 50° to 51° C., standard of the German Pharmacopœia.

**Vanillin.** In this product competition seems to have settled down somewhat. The amount of the consumption of and the demand for it seems to have been by far overrated. It has been left out of consideration that the inventors are always in the advantage, and are under the necessity of maintaining, at their own risk and in their own interest, the continuance of establishments and of an industry instituted by them many years ago.

It deserves also to be mentioned that a vanillin adulterated with acetanilide has recently been observed in the market by Mr. Hefelmann<sup>2</sup>). He found in a vanillin, obtained from Switzerland, nearly 27 per cent of acetanilide, which by its property to readily crystallize is well adapted for application as an adulterant of products like vanillin. Mr. Hefelmann found the adulterated product to melt at 61°, while the melting point of pure vanilline is between 79° and 82°. This is readily and completely soluble in dilute sodium hydroxide solution, the adulterated article only partly. Acetanilide was recognized by the nitrogen determination.

For the separation of the acetanilide, Mr. Hefelmann recommends repeatedly to shake the ether solution of vanillin with concentrated sodium bisulfite solution; the ether solution is subsequently washed with some water and allowed to evaporate. Hereby all vanillin is fixed as a sodium bisulfite double compound and is completely taken up by the water, so that the remaining ether solution contains only the acetanilide. This can readily be identified after the evaporation of the ether. The acetanilide isolated in this way showed its characteristic form of crystallisation, melting at 111° to 113°, separating oil drops of anilin when heated with strong potassa lye, and discharging the strong odor of isonitrile when chloroform was added to this lye. The presence of acetic acid can readily be shown by the well known acetic ester reaction.

In consideration of the examination of this kind of commercial vanillin, the occasional cheap offers should be met with due discrimination. Heretofore such sophistications had been observed in America only (see our Report of October 1896, pages 102 and 103).

<sup>1</sup>) W. Dymock, *Materia Medica of Western India*, 1885.

<sup>2</sup>) *Berliner Apotheker-Zeitung* 1898, No. 49.

12

SEMI-ANNUAL REPORT

OF

SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ

NEAR LEIPZIG

LONDON • NEW YORK.



OCTOBER/NOVEMBER 1905.

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## List of abbreviations.

$d$  = specific gravity.

$d_{20^{\circ}}$  = specific gravity at  $20^{\circ}$ .

$d \frac{20^{\circ}}{4}$  = specific gravity at  $20^{\circ}$ , compared with water at  $4^{\circ}$ .

$\alpha_{D15^{\circ}}$  = optical rotation at  $15^{\circ}$ , in a 100 mm. tube.

$[\alpha]_D$  = specific rotation.

$n_{D15^{\circ}}$  = index of refraction at  $15^{\circ}$ .

$n$  = normal.

$\frac{n}{2} \left( \frac{n}{10} \right)$  = semi-normal or deci-normal (titrated solutions).

gm. = gram; cc. = cubic centimeter; mm. = millimeter.

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Temperatures are uniformly stated in centigrade degrees ( $^{\circ}$ ).

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The most important event since the publication of our last Report, the termination of the war between Russia and Japan, has removed from Trade and Industry a nightmare which became all the more oppressive the longer the hostilities were drawn out, and which, if further prolonged, would have demanded numerous sacrifices from the commercial world. It may confidently be expected that in the era of peace the deep wounds inflicted will soon heal, and that the removal of the political dissensions in the Far East will synchronise with the dawn of a period of economical prosperity for the nations interested, like for all civilised countries of the world.

From the statistics which have meanwhile been published, it can be seen that the German Chemical Industry has again in the year 1904 continued its upward movement.

	<u>1904</u>	<u>1903</u>
Number of Works . . . .	8004	7747
Number of qualified workmen	177461	168950
Amount of wages paid . .	185050509 marks	174402866 marks.

The export of products manufactured by the German Chemical Industry has grown in a corresponding degree. It amounted

in 1904	to 473499000 marks
„ 1903	„ 448244000 „
„ 1902	„ 430441000 „
„ 1901	„ 408366000 „

In our particular branch, the total exports were

in 1904	491000 „ „	6874000 marks
„ 1903	424400 „ „	5942000 „
„ 1902	424700 „ „	5683000 „
„ 1901	388000 „ „	4658000 „
„ 1900	380000 kilos,	value 4634000 „

The fear to which we gave expression at the commencement of 1905 has not come true as far as our branch is concerned; on the

contrary, both the home trade and the export show a higher value in the turnover. For this reason the hope is justified that the current year will end favourably.

The export of German toilet soaps and perfumery has in 1904 again increased slightly, both as regards quantity and value, in comparison with that of the previous year, without, however, reaching the figures of the years preceding 1903.

The quantities and values of the products exported may be tabulated as follows: —

I. Soap in tablets, including scented soap . . . .	4 871 200 kilos, value	6 089 000 marks
II. Fatty oils, scented . .	3 300 " "	18 000 "
III. Scents not containing alcohol . . . . .	149 000 " "	14 000 "
IV. Liquid perfumes, containing alcohol or ether, including hairwashes, dentifrices, and mouth washes . . . . .	1 721 300 " "	5 195 000 "
V. All other perfumes, not otherwise enumerated	481 000 " "	1 298 000 "
VI. Soap and perfumes insufficiently declared .	2 500 " "	11 000 "
<hr/>		
Total in 1904	7 094 200 kilos, value	12 625 000 marks
against in 1903	12 577 000 marks	
" " 1902	15 570 000 "	
" " 1901	15 678 000 "	
" " 1900	15 048 000 "	

The trade with the United States has now for some years been developing strongly. The export of essential oils from Germany was

in 1904	155 000 " "	2 169 000 marks
" 1903	92 000 " "	1 290 000 "
" 1902	73 000 " "	982 000 "
" 1901	54 000 kilos, value	653 000 "

Against this, there were imported into Germany in the fiscal year 1903/1904:

peppermint oil, 22 300 lbs., value	65 500 dollars
other oils	" 124 000 "
<hr/>	
Total	189 500 dollars

The commercial transactions with France have undergone a slight change in favour of the latter country. France exported essential oils to Germany:

in 1901	57 000 kilos, value	1 033 000 marks
„ 1902	62 000 „ „	1 203 000 „
„ 1903	63 000 „ „	1 252 000 „
„ 1904	59 000 „ „	1 294 000 „

whereas the German exports to France show the following figures:

in 1901	59 000 kilos, value	713 000 marks
„ 1902	68 000 „ „	917 000 „
„ 1903	54 000 „ „	756 000 „
„ 1904	44 000 „ „	617 000 „

The customs curiosities in the intercourse with France, to which we referred in the introduction to our last Report, continue without hindrance, as the following decision of the Head Department of the French Customs shows:

Up to the present, heliotropin has been taxed as a “chemical product not specially enumerated, without alcohol base”, according to Tariff number 282 (B). This classification, however, has given rise to objections<sup>1)</sup>, inasmuch as it has been pointed out that this product is only placed on the market by the manufacturer after it has been purified and crystallised by means of alcohol.

The “Comité consultatif des arts et manufactures”, to which the examination of this question has been entrusted, has expressed itself, in the opinion dated December 7, 1904, to this effect, that the manufacture of heliotropin as a matter of fact necessitates the use of alcohol, and that in the proportion of 10 litres to 1 kilo; and that for this reason the product must be classified as a “chemical product not specially enumerated, with alcohol base” under Tariff number 282 (A), and be taxed with an import duty of 80 francs for 1 hectolitre pure alcohol, and a denaturation-tax of 2,42 francs.

This decision has received ministerial assent under date 18<sup>th</sup> January 1905. (Circular of the Head Department of the French Customs No. 3481, of 31<sup>st</sup> January 1905.)

Contrary to this opinion of the “Comité consultatif” in question, we wish to state that no doubt alcohol is employed in the recrystallisation of heliotropin, but that not more than one half litre alcohol is used for 1 kilo heliotropin. At a selling-price of about 15 francs per kilo it is of course out of the question to use larger quantities than that mentioned above. The statement, however, that 10 litres alcohol are employed in the purification of 1 kilo heliotropin, is, as every manufacturer can confirm, simply absurd, and it throws a very bad light on the fitness or the impartiality of the French experts.

<sup>1)</sup> Probably on the part of French competitors.

The sale of our products to Spain, like the entire export to that country, suffers severely from the critical situation there, the chief cause of which must be sought in the total ruin of the viticulture. The preparatory steps taken by the Government for the introduction of the alcohol monopoly, and the opposition set on foot against it, have caused such a panic in this industry and also in the brandy manufacture, that many firms interested in the latter have discontinued this business altogether. The end of this state of affairs cannot as yet be foreseen.

With regard to the duty levied on single copies of catalogues and price-lists entering Australia by post, to which we referred in our last Report, we find the following communication in the German "Handelsarchiv", which confirms this almost incredible measure.

In reply to a question as to the manner in which the duty is levied on single copies of catalogues and price-lists which are introduced into the territory of the Australian Commonwealth, the customs Authorities at Sydney state that, in accordance with instructions from the principal customs Authorities in Melbourne, dated 4<sup>th</sup> November 1904, the duty is to be charged on the following basis:

for a weight up to	3 <sup>3</sup> / <sub>4</sub> ounces	. . . . .	1 <sup>1</sup> / <sub>2</sub> d.
" " " " "	6 <sup>1</sup> / <sub>2</sub> "	. . . . .	1 "
" " " " "	9 "	. . . . .	1 <sup>1</sup> / <sub>2</sub> "
" " " " "	12 "	. . . . .	2 "
" " " " "	14 <sup>1</sup> / <sub>2</sub> "	. . . . .	2 <sup>1</sup> / <sub>2</sub> "
" " " " "	16 "	. . . . .	3 "

The duty is levied in this manner that the postal Authorities affix to the dutiable printed matter a stamp of the value of the duty, which is payable by the addressee, and collect the amount shown on delivery of the printed matter.

The consequence of this is that the acceptance of printed matter is refused by many addressees, at the expense of the senders. It is to be hoped that such a narrow-minded impediment to the commercial intercourse may soon be removed by diplomatic means.

The export to Japan was exceptionally brisk before the recent increase in the customs duties came into force. The conclusion of the peace may give a further impulse to business.

In Mexico the introduction of the gold standard has meanwhile become an accomplished fact. There can be no doubt that the stability and security in business transactions, which is thereby brought about, make this country an even more desirable market than before. Contrary to the foregoing, the commercial situation in Brazil continues to suffer from the uncertainty in the monetary conditions and the credit in that country. The economical situation in the Argentine Republic, as might be expected, has undergone further improvement. The statistics of imports and of exports show considerable increases. If it remains free from internal disturbances, a further favourable development of this country, so rich in natural resources, may be looked for. In Chile

the state of affairs is also likely to improve since the political unrest has come to an end.

The values of many of the leading articles in our industrial branch showed a considerable decline, due partly to overproduction, and partly to the constantly growing competition which now carries on a struggle for life. The former has to be accepted without demur; the latter is the outcome of the spirit of the present time, and must be attributed either to unfairness, or to commercial inexperience. Experience shows that the inferior elements cause but a passing injury to the honest trade, and come to grief on the growing enlightenment of the buying public, a purpose to which these Reports are also mainly devoted. Our research laboratories show almost daily to what extent adulteration takes place, and the amount of cunning with which this obscure trade is carried on, but also that it is finally laid low by the results of diligent scientific research.

With the latter subject, and also with the commercial position of our leading articles, we deal more fully in the following pages which we recommend to the favourable consideration of our readers.

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**Oil of *Achillea nobilis*.** The essential oil of *Achillea nobilis*, which was for the first time produced in 1835 by F. Bley, has been submitted to a chemical examination by P. Echtermeyer<sup>1)</sup>. The oil, distilled from the flowering herb of the plant by Dr. Weppen of Blankenburg am Harz, had the following constants:  $d_{15^\circ}$  0,9363; optical rotation in a tube 200 mm. long —  $20,82^\circ$ ; it distilled at  $170^\circ$  to  $265^\circ$ . The ester content of the oil was 18,2%, calculated for  $C_{10}H_{17}O \cdot CO \cdot CH_3$ ; the acetylated oil had an ester-content of 34,3%, from which, after deducting the quantity of ester present in the original oil, a content of 13,1% free alcohol of the formula  $C_{10}H_{18}O$  is calculated. Neither ketones and aldehydes, nor cineol could be detected. Attempts were next made to convert the alcoholic fraction of the oil into terpenes, and for this purpose the oil was enclosed with zinc chloride and phosphorus pentoxide in a sealed tube. The result, as might be expected, was a resin. In order to prevent resinification, the oil was next slowly brought into reaction at reduced temperature, with phosphoric acid anhydride, and the product thus obtained distilled off *in vacuo*. The terpene mixture distilled over sodium, could be split up into two principal fractions of the boiling point  $153^\circ$  to  $161^\circ$  and  $171^\circ$  to  $177^\circ$ . The first of these contained camphene,

<sup>1)</sup> Arch. Pharm. 243 (1905), 231.

for it yielded isoborneol; in the other no known terpene was discovered. For the detection of the alcohols present in oil of *Achillea nobilis*, 100 gm. of the oil were saponified, and the saponified and dried oil treated with sodium under reduced pressure. After removing by distillation *in vacuo* the portions which had not reacted with sodium, the alcoholates remained behind in the form of a brown resinous mass, and upon distillation with steam yielded an oil containing borneol. The borneol, recrystallised from ligroin, melted at  $203^{\circ}$ , its urethane at  $139^{\circ}$ , and the bromal addition product at  $104^{\circ}$  to  $105^{\circ}$ . In addition to borneol, an alcohol boiling at  $197^{\circ}$  to  $201^{\circ}$  was obtained, which had the odour of linalool, but which on oxidation yielded no citral. The quantity was insufficient for a more detailed examination. A fraction boiling from  $248^{\circ}$  to  $265^{\circ}$  had the composition  $C_{10}H_{16}O$ . In the oil distilled off from the alcoholates, camphene could be detected by conversion into isoborneol; there was also present a hydrocarbon  $(C_{10}H_{16})_n$  boiling at  $240^{\circ}$  to  $245^{\circ}$ .

When acid was added to the saponification liquor of the oil, a small quantity of an oil (not further examined) separated off of which the odour reminded of thyme; this oil did not solidify at  $-15^{\circ}$ , and gave a greyish-green coloration with ferric chloride. The following acids could be detected: formic acid, acetic acid and caproic acid (?).

**Almond Oil, pressed (from apricot kernels).** Our friends in Syria report that this year's harvest of Damascene apricot kernels is a small one. Whilst in good years about 8000 bales are gathered, and in 1904 about 5500, the estimate for this year is only 2000 to 2500 bales. In consequence of this, the farmers are looking forward to high prices, and believe that at least 90 francs per 100 kilos will be reached. Up to the present, however, the principal buyers decline to do business on such terms. At advancing prices, a certain demand has only arisen for the inferior Mersina kernels up to 70 francs, and for Aleppo kernels up to 75 francs. The better-class Tripoli kernels are said to have been sold at 77 to 80 francs.

The further course of the market, and, in conjunction therewith, the prices of the oil, will now only depend upon the demand.

Business in pure pressed oil from apricot kernels was during the whole of last season extremely languid, owing to competition of the most disagreeable kind. We have had repeated opportunities of examining inferior qualities, and would most strongly caution against "cheap" purchases of this article. Contrary to this, there was a continued fair demand for essential oil of bitter almonds, which we could only satisfy by a special effort.

**Almond Oil, pressed (from sweet almonds.)** The market quotations of the remaining unimportant stocks of Puglia and Sicilian

almonds are firm, and the opinion is that the prices of the new fruit will also be high, as large parcels have been sold for forward delivery. How the quotations will move after these engagements have been met, it is impossible to predict, in view of the heavy speculation which usually takes place in this article.

The almond oil pressed by ourselves from best sweet Sicilian fruit is quoted at prices corresponding to the present state of the market.

**Amber Oil.** From the difference between the rotation-constants of d-borneol ( $[\alpha]_D + 3,24^\circ$ ), isolated by Haller from amber, and the d-borneol ( $[\alpha]_D + 38,39^\circ$ ) regenerated by Tshugaeff from xanthogenic acid ester, Rakusin<sup>1)</sup> concludes that the d-borneol isolated from amber must be partly racemised; that the indirectly observed optical activity of amber is "residuary" (what the author may mean by this expression cannot be gathered from the work); and that the material from which the amber was formed, possessed a considerably greater activity. The author believes to have found a direct proof of the foregoing in the amber oil which, as is well known, is obtained by dry distillation of amber; but for the present he confines himself to mentioning the constants ascertained by him, and some properties of this oil, which, however, contain hardly anything new<sup>2)</sup>. Rakusin found the following:  $d_{18^\circ} 0,9217$ ; rotation in a 200 mm. tube  $+ 45,8^\circ$  (degrees of saccharimeter), corresponding to  $+ 15,88^\circ$  circle division. The oil dissolves in two volumes 95 per cent. alcohol; it is further readily soluble in ether, benzene, chloroform, carbon disulphide, and acetone.

**Anise Oil.** With regard to this year's anise harvest in Russia, it is reported from the various districts that at first a well-founded hope existed of a good harvest, as the fields were in very good condition, and moreover a decidedly larger area was under cultivation than in the previous year. But the drought which prevailed almost throughout the producing districts since April, has injuriously affected the development of the plant, and instead of 40 to 50 poods per desjatin, as had been expected, the crop has in all probability hardly exceeded 20 poods. The cultivation this year extends over about 4000 desjatins, and the yield would therefore amount to about 80000 poods or about 1,360000 kilos. This result compares as follows with that of the last three years:

1904	about	120000	poods
1903	"	60000	"
1902	"	280000	"

<sup>1)</sup> Chem. Zeitg. **29** (1905), 669.

<sup>2)</sup> Comp. Report April 1903, 8.

With regard to the probable course of the prices, it is anticipated that owing to the scarcity of old stocks, the speculators will take a very active part in the business right from the beginning. Already some weeks ago speculative buyers visited the peasants who, in consequence, have acquired very inflated notions of the prices. For this reason the first anise market at Krasnoje has greatly disillusioned the purchasers, inasmuch as the supplies were very unimportant, and the prices demanded were high throughout. As a consequence, the anise oil manufacturers and exporters were quite unable to cover their requirements, and on the second anise market, being also scantily supplied, the brisk demand has caused a further advance in the prices.

The first average samples received by us in August had a very unfavourable appearance, and were not green, but rather of a grey colour. The kernel had also developed badly, owing to the dry heat. The samples from the market at Krasnoje which have come to hand are somewhat better, but in any case the quality can only be designated as 'fairly good'.

According to these facts it is probable that the prices of Russian anise oil will experience this season a decided increase.

With regard to the anise harvest in Turkey, no report has as yet been received.

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Our laboratory recently received for approval a sample designated as anethol, which according to the result of the examination was found to be an inferior preparation, and did not even possess the anethol-content of a good anise oil. The crude material for its preparation had been fennel oil. The constants of this product were as follows:  $d_{25}^0$  0,9792;  $\alpha_D + 1^\circ 7'$ ;  $n_{D25}^0$  1,55163; congealing point  $+ 16,8^\circ$ ; soluble in 1,6 volumes 90 per cent. alcohol. The deviations from the properties of pure anethol are therefore very considerable, and it is astonishing that the attempt was made at all to place such a product on the market as anethol.

**Artemisia Oils.** From the laboratory of Edward Kremers, to whom we are already indebted for numerous works dealing with essential oils, originates a work on some new artemisia oils by Frank Rabak<sup>1</sup>). These oils had been distilled in the summer of 1904 from artemisia species collected in South Dakota in August.

1. *Artemisia frigida* Willd., submitted in the fresh state to distillation with steam yielded 0,41% of a greenish oil with a cineol-like odour;  $d_{22}^0$  0,927;  $\alpha_D - 24^\circ 48'$ ; acid number 1,2; ester number 31,8; saponification number 33,0. The dried herb gave on distillation a yield

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<sup>1</sup>) Pharmaceut. Review **23** (1905), 128.

of only 0,07% oil of a darker colour;  $d_{22}^{\circ}$  0,930; acid number 4,7; ester number 40; saponification number 44,7. From the distillation-water of this second distillation, an oil could still be obtained with petroleum ether, which was also darker than the oil from the fresh herb. Rabak states for the extracted oil  $d_{22}^{\circ}$  0,916; acid number 5,3; ester number 25; saponification number 30,3.

2. From the fresh herb of *Artemisia leudoviciana* Nutt. were obtained 0,38% greenish yellow oil with a strong aromatic odour;  $d_{22}^{\circ}$  0,929;  $\alpha_D$  —  $16^{\circ} 14'$ ; acid number 4; ester number 10; saponification number 14.

3. The fresh herb of *Artemisia caudata* Michx. yielded 0,24% yellow oil with a sweetish odour, which points to the presence of methyl chavicol or anethol.  $d_{22}^{\circ}$  0,920;  $\alpha_D$  —  $12^{\circ} 30'$ ; acid number 0; ester number 17,0.

The further chemical examination of the oils will, if possible, be continued next summer, as the quantities of oil hitherto obtained were not sufficient for this purpose.

**Basil Oil.** On the distribution of essential oil in the basil plant, see under Phyto-physiological Notes, page 89.

**Bay Oil.** The extent to which, even at the present day, essential oils are still adulterated, is shown by the examination of a bay oil, of which the results were as follows:  $d_{15}^{\circ}$  0,8857;  $\alpha_D$  —  $3^{\circ} 18'$ ;  $n_{D20}^{\circ}$  1,48122; phenol-content 15,5%; did not make a clear solution with 10 volumes 80 per cent. alcohol; with 90 per cent. alcohol it made at first a clear solution, but with 0,8 volumes, or more, cloudiness resulted. Pure bay oil has the specific gravity 0,965 to 0,985, and a phenol-content of 59 to 65%.

Coarse adulterations of this description are bound to attract the attention of the consumer, and can hardly bring the adulterator a permanent profit, as they can readily be detected in the examination.

**Oil of Birch buds.** Up to the present the composition of birch bud oil, first produced by H. Hänsel<sup>1)</sup> in 1902, was still unknown. H. v. Soden and Fr. Elze<sup>2)</sup> have submitted an oil distilled by Heine & Co. from birch buds, to a more detailed examination, and have detected in it a new sesquiterpene alcohol  $C_{15}H_{24}O$ , which they call betulol. The yield of birch bud oil amounted to 4,3%. When the oil was cooled down to  $-10^{\circ}$ , small quantities of crystals melting at  $50^{\circ}$  separated off, which are probably paraffin. The oil boils between  $265^{\circ}$  and  $295^{\circ}$  with decomposition, inasmuch as acetic

<sup>1)</sup> Chem. Centralbl. 1902. II. 1208.

<sup>2)</sup> Berl. Berichte 38 (1905), 1636.

acid splits off and a strong formation of resin occurs. The specific gravity amounted to 0,975 at 15°;  $\alpha_D - 2^\circ$ ; acid number 2,1; ester number 67,2, corresponding to 31,44 % acetate of a sesquiterpene alcohol  $C_{15}H_{24}O$ ; saponification number after acetylation 177,8, corresponding to 47,4 % of free alcohol  $C_{15}H_{24}O$ . For isolating betulol the acid phthalic ester served which is readily formed when the oil is heated in benzene solution with phthalic acid anhydride. The pure betulol obtained from the phthalic acid compound by saponification with alcoholic potash, shows the following constants:  $d_{15^\circ}$  0,975;  $\alpha_D - 35^\circ$ ; boiling point 138° to 140° at 4 mm., 287° to 288° at 743 mm. pressure with partial decomposition; it is soluble in 3 parts 70 per cent. alcohol; its composition is probably  $C_{15}H_{24}O$ .

When boiled with acetic acid anhydride, betulol is quantitatively acetylated. The acetate boils at 142° to 144° at 4 mm. pressure, and has the specific gravity 0,986 at 15°. The content of free betulol in the oil amounts to about 47 %; in addition to this, the oil appears also to contain the acetic ester of this sesquiterpene alcohol or of other high alcohols.

In connection with the above, we quote here the physical constants of an oil which we distilled some time ago: —

$d_{15^\circ}$  0,9755;  $\alpha_D - 6^\circ 14'$ ;  $n_{D20^\circ}$  1,50179; acid number 1,6; ester number 73,4; acetylation number 170,5. These figures correspond to an ester-content of 34,35 % acetate of a sesquiterpene alcohol  $C_{15}H_{24}O$ , or to a content of free sesquiterpene alcohol of 41,10. The oil had a golden-yellow colour, and dissolved in 1 vol. 80 per cent. alcohol. When an attempt was made to dissolve the oil in a large quantity of 70 per cent. alcohol, a separation of crystals due to paraffin took place.

**Cajeput Oil.** The value of this article has gradually dropped again to a sensible level, since the supplies have once more become larger. The shipments from Macassar, from 1<sup>st</sup> January to 30<sup>th</sup> May of this year, i. e. 5 months, were:

to Europe . . . . .	159 baskets
America . . . . .	14    "
China . . . . .	86    "
Java . . . . .	1082   "
Singapore . . . . .	1027   "

Total 3268 baskets.

The baskets usually contain 25 bottles of 600 grams, i. e. 15 kilo net, so that the total quantity exported amounts to about 35500 kilos.

The bulk of the parcels shipped to Java and Singapore has probably found its way to Holland.

The United States of America are still the largest consumer, and of increasing importance; the quantities imported there were:

in the fiscal year 1904 . . . .	31137 lbs.
" " " " 1903 . . . .	19795 „
" " " " 1902 . . . .	1783 „

In Germany the consumption appears to be on the decline.

**Camphor Oil.** The Japanese are making energetic efforts to bring about a further rise in the prices, but the principal consumers show great reserve, and it is hoped that the present exaggerated demands will be given up.

**Caraway Oil.** The result of the caraway harvest in Holland is estimated by our buyers at about 30000 bales, and is therefore considerably below the average, amounting as it does to scarcely one-third of the quantity gathered in 1904. The individual provinces participate as follows: —

North Holland about . . . . .	20000 bales
Zeeland „ . . . . .	6000 „
Brabant „ . . . . .	3000 „
Friesland „ . . . . .	1000 „

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Total about 30000 bales

The old stocks are estimated at 5000 „

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Quantity at disposal about 35000 bales

The crop is estimated at about 8 bales per acre.

Owing to the great drought of last year, the condition of the fields was so bad that in Brabant almost the whole, and in Zeeland a large proportion of the land was ploughed and cultivated with sugar-beet. In both provinces but very little was sown out, and for this reason there will be next year also only a small quantity of caraway brought on the market.

Although in North Holland the usual area of about 2500 acres has been sown, the plants are thinly distributed, and are weak, so that there also a small harvest must be anticipated in 1906.

Brabant and Zeeland yield in a good year about 40000 bales, but this year not one fourth of that quantity.

Offers from Sweden and Norway move within very narrow limits and are of no importance; the same applies to East Prussia.

The exports from Holland to Germany in 1904 were:

via Hamburg . . . . .	28808 bales
„ Groningen . . . . .	6648 „

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Total 35456 bales of 50 kilos,

whilst in 1903 the export via Hamburg alone amounted to 36682 bales.

The exports of caraway from Russia to Germany amounted in 1903 to 140520 kilos.

According to the foregoing, the advance in the quotations of caraway oil and carvol appears perfectly justified, the more so as the oil-content is considerably lower than in normal years. We do not think we are wrong in assuming that the prices of caraway will experience a further advance, so that it would be a wise step to cover the year's requirements of caraway oil at an early date.

As a consequence of the rise in the prices of caraway oil, we have repeatedly observed in our laboratory adulterations of carvone (carvol). The most striking was a preparation with the following properties:  $d_{15^{\circ}} 0,9339$ ;  $\alpha_D + 53^{\circ} 22'$ ;  $n_{D20^{\circ}} 1,47811$ ; does not make a clear solution with 30 volumes 50 per cent. alcohol. That this carvone, in spite of a detected adulteration with 15 % alcohol (calculated for 90 per cent. alcohol), was so exceptionally deficient in solubility, is very characteristic of the inferior quality of the preparation used as base.

**Cassia Oil.** The value of this important article of Chinese origin was during the last six months again quite normal. No fluctuations in the price of any importance whatever took place, and they appear out of the question since the oil is no longer an object of speculative enterprise at the large seaports, as was formerly the case.

The following interesting statistics may serve as a proof of the opinion expressed above.

Fluctuation in the value of cassia oil  
during the last 20 years (from 1885 to 1905), and quotation on

1 <sup>st</sup>	September	1886	7,—	marks	per	kilo
1 <sup>st</sup>	"	1887	5,80	"	"	"
1 <sup>st</sup>	"	1888	7,10	"	"	"
1 <sup>st</sup>	"	1889	9,—	"	"	"
1 <sup>st</sup>	"	1890	8,80	"	"	"
1 <sup>st</sup>	"	1891	8,60	"	"	"
1 <sup>st</sup>	"	1892	7,70	"	"	"
1 <sup>st</sup>	"	1893	7,40	"	"	"
1 <sup>st</sup>	"	1894	7,60	"	"	"
1 <sup>st</sup>	"	1895	12,—	"	"	"
1 <sup>st</sup>	"	1896	17,—	"	"	"
1 <sup>st</sup>	"	1897	14,40	"	"	"
1 <sup>st</sup>	"	1898	13,40	"	"	"
1 <sup>st</sup>	"	1899	11,50	"	"	"
1 <sup>st</sup>	"	1900	9,10	"	"	"

1 <sup>st</sup>	September	1901	7,70	marks	per	kilo
1 <sup>st</sup>	"	1902	6,30	"	"	"
1 <sup>st</sup>	"	1903	7,20	"	"	"
1 <sup>st</sup>	"	1904	7,40	"	"	"
1 <sup>st</sup>	"	1905	7,—	"	"	"

The above quotations are for best quality oils of 80 to 85 % aldehyde-content, of which small quantities were again available. We recently purchased a parcel which contained as much as 90 %.

The last quotations were:

2/11	for	80 to 85 %	aldehyde
2/8 <sup>1</sup> / <sub>2</sub>	"	75 to 80 %	"
2/7	"	70 to 75 %	"

with a firm tendency of the market, and small stocks in China.

The present position can without hesitation be utilised for large purchases. A strict control of the aldehyde-content is strongly recommended, as our observations have led to the result that in many cases the simple statement of the content cannot be relied upon.

Cassia oil appears now to be placed on the market in a better quality; the parcels which we received last at least pass again the lead acetate test of the German Pharmacopœia. Whether this is a result of our threat that we would refuse all oils suspected of adulteration with colophony or resin, is a matter which we are unable to decide. We hope, however, that in future only unadulterated oils will reach us, as our friends in Hong Kong, who are now provided with the necessary reagents, would there already refuse all adulterated oils.

A sample which we received for approval from London was still adulterated with colophony, and had the following constants:

$d_{15}^{\circ}$  1,0698; acid number 24,67; aldehyde-content 72 %; soluble in 2,3 and more volumes 70 per cent. alcohol, the dilute solution had a strong opalescence; the lead acetate test gave a large precipitate.

**Cedarwood Oil.** From two samples of cedarwood of whose botanical derivation and origin we were unable to ascertain anything definite, we have distilled oils which differ specially from common cedarwood oil by their low specific gravity and their dextrorotation. The microscopical examination showed that the wood was in neither case conifer wood, but was probably derived from cedrela species. The oils which resembled an oil previously distilled by us from cedrela wood from Cuba<sup>1</sup>), had the following constants:

<sup>1</sup>) Gildemeister and Hoffmann, "The Volatile Oils", p. 494. Report April 1892, 41.

Sample I:  $d_{15^\circ}$  0,9134;  $\alpha_D + 15^\circ 50'$ ;  $n_{D20^\circ}$  1,50169; ester number 0,8; ester number after acetylation 18,7; soluble in 6 to 6,5 and more volumes 95 per cent. alcohol; not soluble in 10 volumes 90 per cent. alcohol.

Sample II:  $d_{15^\circ}$  0,9131;  $\alpha_D + 13^\circ 55'$ ;  $n_{D20^\circ}$  1,50142; ester number 0,2; ester number after acetylation 16,7; soluble in 6 to 6,5 and more volumes 95 per cent. alcohol; not soluble in 10 volumes 90 per cent. alcohol.

**Cinnamon Oil, Ceylon.** The prices of fine cinnamon chips have declined since the beginning of the year by about 10%. Our quotations of oil have been reduced proportionately.

As mentioned before, Germany now occupies the first place in the importation of cinnamon. The same is the case with cinnamon chips, of which the shipments from Ceylon in 1904 show the following figures:

to Germany . . . . .	882980 lbs.
America . . . . .	591924 „
Spain . . . . .	489500 „
United Kingdom . . . . .	320893 „
Italy . . . . .	210100 „
Belgium . . . . .	150000 „

The total export had a value of 2871555 marks.

A further drop in the already abnormally low prices is not probable.

**Citronella Oil.** During the last six months the prices have only fallen away very slightly, and not for spot, but for autumn shipments. Prompt oil is in great request, and fetches full prices.

The total shipments from Ceylon during the period from 1<sup>st</sup> January to 31<sup>st</sup> July of this year amounted to 682443 lbs., and are distributed over the different countries as follows:

United Kingdom . . . . .	249490 lbs.
America . . . . .	320908 „
Germany . . . . .	54555 „
Australia . . . . .	41600 „
China . . . . .	8836 „
India . . . . .	1334 „
France . . . . .	5720 „

Total 682443 lbs.,

a figure for 7 months, from which it may be concluded that the quantity exported in 1905 will exceed that of the previous year; the consumption of this perfume is still growing.

The Report of 1904 of the Royal Botanical Garden of Ceylon contains very interesting information on the experiments made in

planting citronella of the *Maha-pangiri* variety. From an area of 1 acre planted in July 1902, the following crops have been gathered:

in March 1904, 10809 $\frac{1}{4}$  lbs., yield of oil about 48 lbs.

in August 1904 8511 " " " " " 36 "

Total in 1904, 19310 $\frac{1}{4}$  lbs., yield of oil about 84 lbs.

This shows that exactly 230 lbs. of grass yielded 1 lb. of pure citronella oil. A further crop from the same acre will be harvested in January 1905. Another plantation produced within 6 months 16083 lbs. grass per acre, with 60 lbs. yield of oil; a third, planted in June, produced in December 9765 lbs. fresh grass yielding 49 $\frac{1}{2}$  lbs. of oil per acre. It is clear from these figures that the citronella cultivation, in view of the low value of the ground and the cheap labour in Ceylon, cannot be so unremunerative as it is frequently represented to be, the more so, as the value of the oil appears to become permanently firmer.

Judging from the citronella oils which have been examined in our laboratory, it seems that the coarser adulterations of the oils with petroleum are now discontinued in Ceylon; at least, we have no longer been compelled to reject oils on account of deficient solubility in 80 per cent. alcohol (Schimmel's test). On the other hand, there was a large number of oils which did not pass Schimmel's raised test. The latter, as is well known, requires that citronella oil after 5% Russian petroleum is added, shall show nearly the same solubility as the pure oil; especially, after diluting 1 volume of the oil mixed with petroleum with 10 volumes 80 per cent. alcohol, no separation of small drops of oil shall be noticeable. The oils which did not pass this raised test were also almost throughout inferior on account of their low geraniol-content, which was found down to 51,6%.

Worse adulterations which we have observed, were this time of quite a different character. A sample sent to us from Marseilles, which was suspected on account of its low specific gravity, was found to be adulterated with 11,2% alcohol. This sample had the following properties:  $d_{15^{\circ}}$  0,8899;  $n_D$  — 9°15'; total geraniol 67,3%; soluble in every proportion in 80 per cent. alcohol; the dilute solution had a faint opalescence. By simply extracting with a solution of common salt, the alcohol added was abstracted from the oil, and consequently the total content of geraniol was lowered considerably, as previously the alcohol had naturally been included in the calculation of geraniol. The properties of the extracted oil were as follows:  $d_{15^{\circ}}$  0,8969;  $n_{D20^{\circ}}$  1,47166; 58,6% total geraniol; soluble in 0,5 and more volumes 80 per cent. alcohol; the dilute solution had a faint opalescence.

Of much more interest was another case where it was a question of an oil which was said to have spoilt the soap in a silk factory. Whether the fault was exclusively due to the oil in question we are unable to say, as we are not acquainted with the other circumstances. But this much is certain, that the examined oil was largely adulterated with lemon oil terpenes. The result of the examination was as follows:  $d_{15^{\circ}} 0,8852$ ;  $\alpha_D + 11^{\circ} 44'$ ;  $n_{D20^{\circ}} 1,47235$ ;  $29,6\%$  total geraniol; not soluble in 10 volumes 80 per cent. alcohol. For comparison we also quote the values accepted as normal for Ceylon citronella oil:  $d_{15^{\circ}} 0,900$  to  $0,920$ ;  $\alpha_D$  to the left up to  $-21^{\circ}$ ; total geraniol at least  $57\%$ .

**Clove Oil.** We find of Reports from the British vice-consul in Pemba, that the yield of the clove-harvest in 1904 reached the exceptional height of 14 447 600 lbs.,

against 5 532 700 in 1903,

and 7 462 300 in 1902.

This high amount, added to the favourable prices obtained, was advantageous for all persons connected with this industry, and also for the two islands (Pemba and Zanzibar), for which the year 1904 has indeed been a period of the greatest prosperity. There had usually been scarcity of labour in the clove-harvest, but this time 500 natives had been brought over from the continent for a period of 3 months, and the effect of this was that every inhabitant of the islands able to work, and even artisans such as masons, carpenters, etc., now took part in the gathering of the cloves. It is only due to this step that the enormous yield of nearly  $14\frac{1}{2}$  million lbs. could be safely gathered within a comparatively short time.

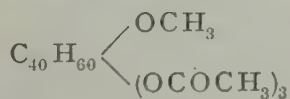
This quantity was considerably larger than the original estimate, and caused the well-known fall which reached in January its lowest level with about 22 florins, or 38 marks per 50 kilos. But after a very few weeks the speculators took hold of this article, and drove it, partly by leaps and bounds, up to 37 fl. or about 63 marks per 50 kilos. This high quotation is not justified by the figures of the last harvest, and may possibly not be maintained, the more so, as the stocks in Holland and London show an increase as compared with the same period of 1904. It is to be regretted that the value of cloves since the opening of the Dutch terminal market, is no longer, as previously, influenced by healthy factors, but is determined by the whims of speculators. It affects the prices of clove oil, and renders our position as advisers of many of our clients extremely difficult.

Caryophyllin, a vegetable crystallisable substance which is present in the closed flower-buds of the clove (*Caryophyllus aroma-*

*ticus* L.), is said to be of the composition  $C_{10}H_{16}O$ . H. Meyer and O. Höning Schmid<sup>1)</sup> have commenced a detailed examination of this body, in order to determine its constitution. The caryophyllin isolated by them according to the well-known methods, and purified as much as possible by repeated recrystallisation from boiling alcohol, melted in a closed tube at  $295^{\circ}$ , sublimed *in vacuo* without decomposition, was readily soluble in ether and hot alcohol, insoluble in water and alkalis, and had the composition  $C_{10}H_{16}O$  already ascertained by previous authors. Owing to the high melting point of the substance, the molecular weight of caryophyllin had already previously been taken to be double or four times the formula disclosed by the analysis.

With the view of deciding this question Meyer and Höning Schmid submitted the purified substance to determinations of the molecular weight, which showed for caryophyllin the molecular quantity  $C_{40}H_{64}O_4$ , i. e., four times that of  $C_{10}H_{16}O$ . In this molecule 4 hydroxyl-groups must be present, for on acetylation an acetyl product  $C_{40}H_{60}(O \cdot COCH_3)_4$  was formed, of the melting point  $268^{\circ}$  to  $271^{\circ}$ . Determination of the molecular weight gave the number corresponding with this formula. Caryophyllin was very stable towards potassium permanganate, but with fuming nitric acid caryophyllinic acid was obtained, which had already been produced by Mylius. This represents a powder which on exposure to the light gradually acquires a yellow or red colour, and which could not be purified by recrystallisation. Titration of the sodium salt of this acid proved the presence of 4 carboxyl groups, a fact which was confirmed by conversion of the salt into a tetramethyl ester  $C_{40}H_{60}O_4(OCH_3)_4$  of the melting point  $159^{\circ}$  to  $160^{\circ}$ . This ester was formed when the silver salt of caryophyllinic acid was boiled with methyl iodide; a by-product soluble in alkali was then also formed, but this also contained methoxyl-groups. Methyl ester of caryophyllinic acid was also produced when the acid was covered with diazo-methane, but in that case the melting point lay at  $164^{\circ}$  to  $165^{\circ}$ .

Caryophyllinic acid could be acetylated, and yielded an acetyl-product of the melting point  $200^{\circ}$  to  $204^{\circ}$ . Diazo-methane also acts on caryophyllin, but a product was then formed whose methoxyl-content was found to be a little too high for a monomethyl ether. The fact that this compound melting at  $187^{\circ}$  represented a monomethoxyl derivative, was proved by its behaviour during acetylation. The acetyl-compound was a triacetyl-product, viz.,



of the melting point  $212^{\circ}$  to  $213^{\circ}$ .

<sup>1)</sup> Monatsh. f. Chemie **26** (1905), 379.

The above treatise induced J. Herzog<sup>1)</sup> to publish the results of his work on caryophyllin which also was not yet completed. He obtained from caryophyllin a diphenyl urethane melting at 137° to 138°



and by boiling with acetic acid anhydride a diacetyl product, whilst Meyer and Hönigschmid thereby obtained a tetra-acetyl product. These two derivatives no doubt also support the formula  $\text{C}_{40}\text{H}_{64}\text{O}_4$  ascertained by Meyer and Hönigschmid, but Herzog points out that he did not succeed in producing pure caryophyllin solely by recrystallisation from alcohol; on the contrary, the apparently pure product crystallised from alcohol, left a brown residue when dissolved in ether, and the portion dissolved in ether showed a smaller content of carbon than the formula  $\text{C}_{40}\text{H}_{64}\text{O}_4$  requires. Contrary to Meyer and Hönigschmid, Herzog found that caryophyllin, when shaken with alkalies, forms salts; he obtained, for example, a potassium salt and a baryum salt, which could be recrystallised from alcohol. Further, when caryophyllin was oxidised with chromic acid in glacial acetic acid, an amorphous acid was formed, which may possibly be identic with Mylius' caryophyllinic acid; but in addition to this he obtained a by-product insoluble in alkali, which yielded an oxime and semicarbazone. With benzoic acid anhydride, caryophyllin formed a benzoyl product of the melting point 173° to 185°.

**Copaiba Balsam Oil.** C. M. Kline<sup>2)</sup> reports on African copaiba balsam, the use of which as a remedial agent is not permitted by most pharmacopœias, and he advocates, on the strength of chemical and therapeutical experiments, the possibility of the medicinal application of African copaiba balsam. The balsam occurring in commerce is a thick liquid with a pungent odour, which contains more than 10% water and contaminations; its specific gravity is 0,9916 to 0,9996. In the pure state the balsam has a dark-brown colour, passing over into reddish, and a strong fluorescence; its odour differs from that of other balsams. After prolonged standing crystals separate out from the African balsam, which probably consist of oxycopaibic acid. By means of steam distillation, Kline obtained from the balsam 43,5 to 45,5% essential oil with a yellow colour;  $d_{15}^{\circ}$  0,928;  $\alpha_D + 5^{\circ} 45'$ . African copaiba balsam is said to be less disagreeable to take than other copaiba balsams, but its action is less powerful. It has been successfully prescribed in cases of prostatitis, recent and chronic urethritis, stricture, and pyelitis.

<sup>1)</sup> Berichte d. deutsch. Pharm. Ges. **15** (1905), 121.

<sup>2)</sup> Americ. Journ. Pharm. **77** (1906), 185.

**Coriander Oil.** The position of this article may in the course of this season become still more critical than last year, as failure of the harvest has taken place in Thuringia and Morocco. The production of Moravia has dwindled down to minute dimensions. For this reason the market will depend exclusively upon the Russian seed, the crop of which is said to amount to about 30 truck-loads, or say 300 000 kilos, a quantity which is not by a long way sufficient for the world's requirements. Under these conditions coriander oil may become dearer as the season advances.

**Erigeron Oil.** Frank Rabak<sup>1)</sup> has supplied a contribution to the knowledge of erigeron oil. In the summer of 1904 he distilled, in addition to other herbs growing wild in South Dakota, also the herb of *Erigeron canadensis* L., popularly known as "fireweed". The fresh herb yielded 0,66% oil of a bright-yellow colour and a peculiar odour reminding somewhat of caraway. A few hours after distillation, crystalline separations were observed; when small quantities of oil were left exposed to the atmosphere, crystals were formed, which were recrystallised from alcohol.

The herb gathered in Madison and dried, yielded on distillation only 0,26% oil. It had a darker colour, and possessed a powerful aromatic odour; when left standing exposed to the atmosphere no crystals separated out from this oil, as it was apparently less pure. The constants ascertained by Rabak were as follows:

	Oil from the fresh herb	Oil from the dried herb
$d_{22}^o$	0,8614	0,8610
$\alpha_D$	+ 67° 16'	+ 76° 37'
acid number	0	0
ester number	108	52
saponification number after acetylation	108	86
aldehyde-content (calculated as citronellal)	0,77%	0,44%

The above table shows that the specific gravity does not indicate whether the oil has been distilled from the fresh or from the dried herb. The higher rotatory power of the oil from the dried herb appears to be due to the fact that some constituents decompose during drying; the corresponding lower ester number confirms this assumption. Free alcohols could only be detected in the oil from the dried herb,

<sup>1)</sup> Pharmaceut. Review **23** (1905), 81.

and that calculated as terpineol 10.9<sup>0</sup>/. This apparently supports the view that the terpineol found in erigeron oil is a product of decomposition. The oils contained small quantities of aldehydes of which nothing further is known; for the calculation citronellal C<sub>10</sub>H<sub>18</sub>O was taken.

## Essential Oils, Sicilian and Calabrian.

Our authority Mr. Eduardo Jacob of Messina, has again rendered us valuable assistance at the time of writing the present Report, and he gives us interesting information<sup>1)</sup>, on the state of the market of these important articles, of which the principal part will doubtless, as usual, be welcome to the majority of our readers.

In consequence of the large stock of essences which had accumulated abroad, and chiefly in America, owing to the heavy exports of the year 1904, the shipments during the first eight months of this year show a rather large decrease as compared with the same months of the previous year, as is shown by the following figures.

The export amounted:

	1905	1904	1903
in January to	89548	105877	95975 kilos
„ February „	80780	98897	97646 „
„ March „	80157	91132	78390 „
„ April „	68657	74955	67319 „
„ May „	53032	57932	62452 „
„ June „	59726	84283	36404 „
„ July „	48219	52584	52173 „
„ August „	43339	47074	46340 „
Total	523458	612737	536702 kilos.

Whilst the total fall in the exports from 1904 to 1905 amounts therefore to 89279 kilos, or almost 15<sup>0</sup>/, the individual countries participate in this reduction in varying degree. Thus, the exports of the months in question of the year 1905 as compared with the same period in 1904, have declined

to America	by about	63200 kilos, or about	22 <sup>0</sup> /
„ the United Kingdom	„ „	20800 „ „	12 <sup>0</sup> /
„ France	„ „	2500 „ „	9 <sup>0</sup> /

whereas those to Austria (for Germany) have increased by about 12300 kilos, or say 32<sup>0</sup>/.

<sup>1)</sup> This special report reaches us at the same time as the news of the terrible earthquake in Calabria and Sicily; so that the possible effect of this natural phenomenon on the production and state of the market has not yet been taken into account in it.

**Bergamot Oil.** In our Spring Report it was already mentioned as probable, that in spite of the smallness of the stocks, and the fact that they were mostly held by persons well provided with capital, the prices of this oil would experience a backward movement. This has actually taken place, and that, because the holders, influenced by the favourable development of the blossoms of the bergamot trees, for a time lost all hope of disposing of their goods at the higher prices which correspond more with this year's situation, and were consequently more inclined to sell.

Buyers abroad have availed themselves as much as possible of these cheap quotations, and made heavy purchases during that period.

Yet in the long run the scarcity of large stocks was bound to make itself felt again, and the prices gradually rose again to the present level, at which they will no doubt remain until the time of the new harvest, provided the demand does not become too strong.

The present stocks are estimated at barely 2500/3000 kilos and will certainly be used up for the greater part in the course of the next few months, before the new oil-harvest comes in.

Widely differing estimates of the prospects of the new bergamot harvest are made in the different districts. Whilst at first on the whole a good inflorescence was reported, and the prospects in the southern districts, i. e. to the south of Reggio, are at the present time still considered fairly good, the trees to the north of Reggio and in the gardens at higher altitudes have suffered much from the weather-conditions during the summer, and in those districts the prospects of the harvest are designated as downright bad. On the average a medium harvest is hoped for, which may turn out more or less rich, according to the oil-yield of the fruit.

Under these conditions the prices of the new oil will probably come somewhat lower than in the previous year, at least at the commencement of the season.

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In the course of the last half year, lemon oil, or lemon oil terpenes, again formed a favourite adulterant of bergamot oil. Although it is difficult to supply a direct proof of such adulteration when the admixture is but small, it is yet possible to conclude with certainty, from the practically always correspondingly altered constants of the oil, that an admixture of lemon oil, or lemon oil terpenes, has taken place. In the tables quoted below (Nos. 1 to 4) we give the results of the examination of a few oils adulterated in this manner. As a coarse adulteration, we could once more after a long time observe turpentine oil (No. 5 of the table). But the most incredible adulteration was supplied by a firm in Messina, who in the most wanton manner placed on the market as bergamot oil, coloured lemon oil terpenes to which

perhaps 5% bergamot oil had been added. It is impossible to give too much publicity to such an adulteration. The constants of this miserable clumsy work are mentioned in the table under No. 6.

As in our last Report<sup>1)</sup>, we now quote at the head of the results of the examinations of the inferior and adulterated oils, the limits of value observed by us on unobjectionable oils, so that everyone may be able to form an opinion on the value of the oils.

	$d_{15^{\circ}}$	$\alpha_D$	% linalyl acetate	Distillation residue
Pure bergamot oil	0,881 to 0,886	+ 8° to + 24°	34 to 40	4,75 to 6%

#### Inferior and adulterated bergamot oils

1.	0,8777	+ 29° 30'	30,0	5,2%
2.	0,8760	+ 30° 38'	27,6	4,4%
3.	0,8771	+ 27° 56'	29,5	4,4%
4.	0,8792	+ 24° 44'	31,0	5,0%
5.	0,8727	+ 16° 56'	15,0	3,8%
6.	0,8583	above + 45°	1,88	0,3%

G. Romeo and G. Moricca discuss in a treatise<sup>2)</sup> which they were kind enough to send us, the method of production of bergamot oil, its physical constants, and the adulterants which come chiefly under consideration. The influence of an adulteration of bergamot oil with oils of turpentine and lemon on the rotatory power is the subject of a particularly detailed examination. The method published by Soldaini and Berté, which consists of this, that one third of the oil is distilled off, and the rotation of this fraction and of the residue is determined, is rejected by Romeo and Moricca, as adulterated oils also come within the limits of value given. They therefore recommend that from 30 cc. bergamot oil, fractions of 5 cc. each be distilled off, and the rotations be determined, especially of the two first fractions. In the case of pure oils the rotation of the first fraction is larger than that of the second; with adulterated oils the reverse is the case. Another examination-method also recommended by Soldaini and Berté, according to which in the case of pure bergamot oils the rotation of the first third is said to be  $2\frac{1}{2}$  times that of the original oil, is corrected by the authors to this extent, that with pure oils the ratio of the rotation of the first third to that of the original oil is all the

<sup>1)</sup> Report April 1905, 31.

<sup>2)</sup> Sull' analisi della essenza di bergamotto, Messina 1905.

greater, the lower the rotation of the oil is. The relative data of genuine oils, and of oils adulterated with turpentine oil and lemon oil, are given in tabulated form.

The determination of density, optical rotation, evaporation residue, and ester-content are probably of greater value for the correct valuation of bergamot oil, than the processes described above, which are based upon somewhat scanty observation material, the more so as the values observed for genuine and adulterated oils differ but little from one another.

**Lemon Oil.** In our last Spring Report we discussed already in detail the combination of landed proprietors and manufacturers which originally formed for the protection of the industry of inspissated lemon (ice and citrate of lime) had extended its operations also to the article lemon oil.

In the course of the last six months the activity of this combination has unfortunately become a factor, not for the consolidation and support of the market, but for unsettling it.

As, namely, the combination, by availing itself of the situation during the spring (then favourable for their purposes), had readily succeeded in raising the article from its lowest level of 4,40 marks to the healthy price of 5,25 marks, its managers were unfortunately tempted to drive up the price still further, namely up to 5,75 marks, which figure was reached in the middle of April.

When, however, the most pressing requirements of the market had been covered, the buyers withdrew altogether, and the consequence was that the price went back to almost the old level, at which it remained, with unimportant sales, up to June.

The combination made a second attempt, early in July, to influence the state of the market, by compelling its members not to sell below 5,25 marks at first, and 5,75 marks subsequently. The total quantity of unused stocks was estimated at that time at about 100 000 kilos, of which perhaps two thirds were controlled by the combination.

As is always the case in such sudden movements of the price, a number of Messina export firms were again taken unawares, and had to pay the prices asked.

But this time the combination was not destined to carry through the exaggerated demands, as the manufacturers and proprietors not belonging to the combination availed themselves cheerfully of this opportunity to dispose of their goods at the comparatively high prices, though always slightly below the prices asked by the combination. The supply of this free essence was so important, that once more a reaction against the high demands of the combination took place, and the prices again dropped to 5,— to 5,25 marks, in spite of the fact that the

important quantities of oil controlled by the manufacturers' union, which are still estimated at about 60 000 kilos, remain withdrawn from the market.

It is reported that among the members of the combination a strong feeling of dissatisfaction against the managers is manifested, as the former begin to lose the hope that the market will be forced to pay the high prices demanded before the new crop comes in. Such doubt would seem to be perfectly justified if it is taken into consideration that apart from the 60 000 kilos of the combination, a further quantity of about 40 000 kilos oil is still held by the manufacturers and exporters, and that this will presumably meet the export requirements for the next few months, until the time of the new harvest.

In view of this discontent, and the unfavourable results shown in the management of the combination, it is at this moment impossible to predict whether and in how far the combination in the coming harvest will be able and willing to interfere with the course of the article lemon oil.

With regard to the coming harvest, it is at the moment impossible to give any more detailed information. In Sicily it is believed that on the whole a medium harvest may be anticipated, and owing to the absence, or rather the great falling-off in the Spanish crop, a brisk trade in lemons in cases is expected, on account of which the prices of the fruit on the trees are very high.

On the other hand, it is not improbable that part of the oil still in stock will be carried over into the new manufacturing season.

Under these circumstances it is believed that the prices of lemon oil during the new harvest season will move between 4,50 and 5 marks per kilo.

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As a new source of supply for lemon oil, California may in the course of time possibly enter the field. We have received from there an oil from the ripe fruit, said to have been pressed by hand, which no doubt slightly differs in its constants from the ordinary lemon oil (which, as is well known, is usually pressed from the not quite ripe fruit), but which possesses a very pleasant odour. This oil has a somewhat darker colour than the Sicilian oil. The constants were as follows:  $d_{15^{\circ}} 0,8598$ ;  $\alpha_D +53^{\circ} 56'$ ;  $\alpha_D$  of the first 10% of the distillate  $+48^{\circ} 42'$  (boiling point  $165^{\circ}$  to  $175^{\circ}$ );  $n_{D20^{\circ}} 1,47490$ ; evaporation-residue 3,6%. For the present it is an open question whether the comparatively low rotatory power of the oil must be attributed solely to the degree of ripeness of the fruit pressed.

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With regard to Berté's new indirect method of determining the aldehydes in lemon oil, mentioned in our last Report<sup>1)</sup>, we have now

<sup>1)</sup> Report April 1905, 35.

before us more detailed work by this author<sup>1)</sup>, so that we are now in a position to report more fully on the subject. Berté determines in the first place the polarimetric deflection of the oil, and subsequently the deflection of the oil after removal of the aldehydes by means of potassium bisulphite solution, the process being carried out as follows: —

"In an Erlenmeyer flask of nearly 250 cc. capacity, 10 cc. oil and 50 cc. of a saturated potassium bisulphite solution are introduced; the flask is closed with a perforated cork through which passes a glass tube 40 to 50 cm. long. The mixture is now shaken until an emulsion is formed, and kept for 10 minutes on a boiling water-bath with repeated shaking, care being taken not to raise the temperature too much. It is then left to cool, again heated for 5 minutes while strongly shaken, and then once more left to cool. The mixture is now placed in a separating funnel, of 100 cc. capacity; after a fairly long rest the upper layer, consisting of the oil, is poured off from the lower one which contains the combined aldehydes. The decanted terpene is twice washed with some distilled water, then filtered off with the addition of a small quantity of anhydrous sodium sulphate, and polarised as soon as it has become thoroughly clear."

From the results of two optical determinations made at equal temperatures, the quantity of the aldehydes contained in the oil is calculated according to the formula

$$C = \frac{100 (A - a)}{A}$$

in which  $a$  represents the rotation of the original oil,  $A$  that of the oil freed from aldehydes, and  $C$  the quantity of aldehydes in per cent. In examinations according to this new method, Berté found for pure lemon oils an aldehyde-content of 6,85 to 7,4 %.

The author endeavours to prove the usefulness of this method by experiments made with mixtures of citral and limonene. In mixtures containing 1 to 10 % citral, Berté found the citral-content again by his new method of determination with an accuracy which fluctuated between 0,03 % too little and 0,16 % too much.

This new process is also recommended by Berté for the aldehyde-determination of terpeneless oils.

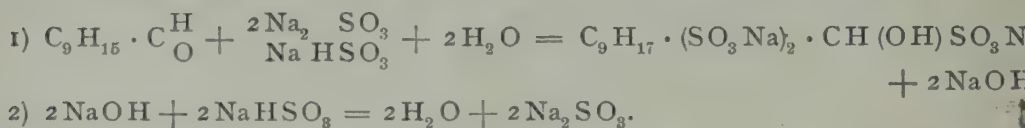
We are pleased to be able to state here that Berté himself now rejects the method<sup>2)</sup> recommended by him and Soldaini for the detection of adulterations with lemon oil terpenes, as lemon oils to which even 30 or 40 % terpenes have been added, may answer the requirements of the distillation method. In our Report of October 1904

<sup>1)</sup> Chem. Zeitg. 29 (1905), 805; Chemist and Druggist 66 (1905), 682.

<sup>2)</sup> Report October 1904, 29.

we have already shown that the process by which 50% of the oil is distilled off, and the rotations of the oil, the distillate, and the residue are then compared, is a failure. Child and Spencer<sup>1)</sup> have affirmed this. Determinations made by them according to the new method gave satisfactory results; the polarimetric method appears to be specially suitable for the citral-estimation in terpeneless lemon oils. The London Essence Co.<sup>2)</sup> express an opinion to the contrary on Berté's new method; they have given up this same method as unreliable already in 1898, because the complete absorption of the citral by the potassium bisulphite solution not only depends upon the time, but also on the manner of shaking. As we have not yet sufficient material at our disposal to express a definite opinion on this new method, we will return to this determination in our next Report.

Shortly before going to press we received from G. Romeo a reprint<sup>3)</sup> in which the author reports on a new method for the quantitative estimation of citral. It is based on this, that citral reacts with a solution of neutral and acid sodium sulphite, with formation of sodium citral-trihydrotrisulphonate according to the following equations:



According to this, three acid equivalents correspond to one molecule citral. For carrying out this experiment, a solution of 400 gm  $\text{Na}_2\text{SO}_3 + 7\text{H}_2\text{O}$  in 1 l water + 160 cc. of a saturated solution of potassium bisulphite<sup>4)</sup>, is neutralised with semi-normal potash, the f. i. 25 cc. of this solution heated with 5 cc. lemon oil, the quantity of acid used ascertained by titration (as indicator rosolic acid is recommended), and the citral-content calculated from this. Experiments were made with pure citral, mixtures of citral and xylene of known citral content, and essential oils containing citral (ordinary and terpeneless lemon oil). The results obtained by the author agree well with one another. Four different lemon oils showed a content of 3,64 to 4,48% citral.

It will be seen that this method is very similar to the determination of aldehydes and ketones recommended by Sadtler. We<sup>5)</sup> were compelled to reject the use of Sadtler's method for the estimation of citral in lemon oil, because an exact titration could not be carried

<sup>1)</sup> Chemist and Druggist 66 (1905), 713.

<sup>2)</sup> Chemist and Druggist 66 (1905), 744.

<sup>3)</sup> Un nuovo metodo di determinazione quantitativa del citral. Messina 1905.

<sup>4)</sup> For practical purposes, the author recommends sodium bisulphite solution.

<sup>5)</sup> Report April 1904, 48.

out. According to our experiments, the present method suffers from the same drawback. We did not even succeed in neutralising the solution distinctly according to the directions given.

**Mandarin Oil.** Last year's oil has been used up entirely, and finally fetched up to 38 marks per kilo.

The prospects of the new harvest do not appear to be favourable.

E. Berté and S. Gulli<sup>1)</sup> have occupied themselves with the examination of mandarin oil. The trees from the fruit of which the oil is pressed, are *Citrus madurensis*, *Citrus deliciosa*, and *Citrus bigaradia sinensis*. Every 1000 fruits yield about 400 gm. oil, whose specific gravity at 15° fluctuates between 0,854 and 0,858; it possesses a rotatory power of  $+67^\circ$  to  $+73^\circ$ . On account of its high price, mandarin oil is frequently adulterated with oils of sweet and bitter orange, lemon oil and terpenes. For the purpose of detecting adulterants of that kind in mandarin oil, the authors now recommend the well-known method of fractional distillation of Soldaini<sup>2)</sup> and Berté, which, however, has recently<sup>3)</sup> been rejected by the latter as useless for testing lemon oil. This method consists of this, that of the oil to be examined 50% are distilled off, and the rotations of the original oil, the distillate, and the residue are compared with one another. Pure mandarin oil, according to the results mentioned, yields a distillate which rotates  $3^\circ$  to  $3^\circ 10'$  higher, and a residue which rotates  $3^\circ 10'$  to  $3^\circ 30'$  lower than the original oil. In the case of adulterated oils (unfortunately no definite data are given of the proportionate quantities) Berté and Gulli found the rotation of the distillate  $1^\circ 30'$  to  $2^\circ 45'$  higher, and the rotation of the residue  $1^\circ 20'$  to  $3^\circ 58'$  lower than the rotation of the original oil. As the observations which the author mentions are not sufficient to form a conclusive opinion on the usefulness of this method for mandarin oil, further repeated tests are required, which it is our intention to carry out in our laboratory.

**Orange Oil, bitter.** The prices of this oil have remained very firm during the summer months for first qualities, although the demand was slow; it is believed that something like 1000 kilos, divided over many holders, are still in stock in Sicily.

The prospects of the coming crop, however, are unfavourable; it is estimated at about  $\frac{3}{5}$ <sup>ths</sup> of last year's production, so that the prices

<sup>1)</sup> According to reprint sent: "Sull' analisi della essenza di mandarino", Messina 1905.

<sup>2)</sup> Report October 1904, 29.

<sup>3)</sup> See present Report, page 29.

will no doubt remain fairly high, even at the commencement of the new harvest.

Although bitter orange oil, as is well known, experienced very important fluctuations in the price in the course of last year, it reached us almost without exception only in the pure state. Only once were we able to detect in our research laboratory a more or less coarse adulteration with resin. The oil in question was at once suspected on account of its large evaporation-residue, and the high specific gravity due to this. The constants of this sample which originated from London were:  $d_{15^\circ}$  0,8976;  $a_D + 79^\circ 35'$ ;  $a_D$  of the first 10% of the distillate  $+ 94^\circ 46'$ ; evaporation-residue 12,4%; it had a resinous character, the acid number 22, and the ester number 106.

**Orange Oil, sweet.** The brisker demand for orange oil which occurred in May, added to the not very favourable reports on the blossoming of the trees, gradually drove the prices of this oil up to 15,50 marks, at which level it maintained itself for some time, but finally in the course of July and August, fell back again to 14,50 to 14,25 marks.

The cause of this decline is to be found in this, that after the brisk trade in May, a quiet time followed, during which business in this article came almost entirely to a standstill, so that the owners who otherwise about this time are in the habit of carrying their nose very high in the air, were now more willing to reduce their prices.

The stocks of old oil are very short, and are estimated at 2500 to 3000 kilos, of which probably only the smallest portion will be carried over into the new producing season.

With regard to the new harvest, the prospects of same are unfortunately very bad. In the course of the summer it has become more and more apparent, that the orange trees in Calabria have suffered very much from the severe frosts during the winter. The quantity of fruit is estimated at only about one half of the previous year's crop. In the Sicilian orange gardens the prospects of the harvest were at first not so bad as in Calabria, but in the course of the summer they grew more and more modest owing to the large quantity of young fruit that fell from the trees, and it will now be necessary to reckon there also on a much reduced crop.

A further factor in favour of higher prices is this, that the reports concerning the orange harvest in Spain are also, owing to the after-effects of the winter frosts, equally unfavourable, if not more so, than in Calabria; in consequence of this, the Sicilian fruit merchants are anticipating a large demand for fresh oranges from foreign buyers who in late years have been importing increasing quantities of Spanish oranges, and who are therefore prepared to pay exceptionally high prices for the fruit on the trees.

As the export of oranges has been comparatively slack this year, can scarcely be expected that any stocks worth mentioning will be sold abroad by the commencement of the new harvest.

Unless, therefore, appearances are entirely deceptive, a very small production of oil and a brisk demand may reasonably be expected.

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**Eucalyptus Oil.** At the present time Australia again controls the market in the oils rich in eucalyptol; no other source of supply can compete permanently against such enormous production. Portugal supplies a few thousand kilos, but Algeria has been completely supplanted and has now for some years only taken a very feeble part in the competition. The present value of best rectified oils of the globulus species, with a guaranteed eucalyptol-content of 60%, is exceptionally low.

In the oils containing phellandrene, Australia has from the first been without rival, and in view of its renowned productive power need fear no competition. The use of these kinds is limited.

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We have already on a previous occasion<sup>1)</sup> observed the presence of an alcohol in the last fraction of the oil of *Eucalyptus globulus*. This alcohol has recently been submitted by Wallach<sup>2)</sup> to a more detailed examination. The alcohol, purified by the acid phthalic ester (action of phthalic acid anhydride on the sodium compound of the alcohol in ethereal solution), had the following constants:

boiling point 92° (at 12 mm. pressure);  $d_{20} 0.9745$ ;  $n_{D20} 1.49630$ ;  
 $[\alpha]_D - 52.45^\circ$  in 12.75 per cent. solution.

It has the composition  $C_{10}H_{16}O$ , and greatly resembles in its properties the pinocarveol<sup>3)</sup> obtained synthetically by Wallach. The phenylmethane of the alcohol could be split up into two components, of which one melted at 94° to 95°, and the other at 82° to 84°. By oxidation with chromic acid there was formed from the alcohol a body  $C_{10}H_{14}O$ , which yielded two semicarbazones (melting point 209° to 210°, and about 320°). The oxime boiled at 140° (20 mm. pressure) and on cooling congealed in a crystalline form.

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We have repeatedly discussed in our Reports<sup>4)</sup> individual numbers of J. H. Maiden's excellent work "A critical revision of the genus *Eucalyptus*". At the moment we have before us the sixth number<sup>5)</sup>,

<sup>1)</sup> Gildemeister and Hoffmann: "The Volatile Oils", p. 528.

<sup>2)</sup> Nachr. k. Ges. Wiss. Göttingen **1905**, Part. I, 3.

<sup>3)</sup> Liebig's Annalen **277** (1893), 149; **249** (1888), 387.

<sup>4)</sup> Report October **1903**, 37; October **1904**, 39; and April **1905**, 37.

<sup>5)</sup> Sydney **1905**.

embellished with 4 pages of good illustrations. In this number the following species are discussed at great length:

1. *Eucalyptus amygdalina* Labillardière [synonyms: *E. salicifolia* Cav., also *Metrosideros salicifolia* Soland., *E. angustifolia* R. Br., *E. tuberculata* Parm., *E. radiata* Sieber., *E. purpurascens* Link with var. *petiolata* D. C., *E. globularis*, *E. glandulosa* Desf., *E. Lindleyana* D. C., *E. longifolia* Lindl., *E. gracilis* Miq., *E. tenuiramis* Miq. with var. *numerosa*, var. nov. (vel *E. numerosa* sp. nov.), *E. amygdalina* Labill. var. *radiata* Benth. (partim), *E. calyculata* Link., *E. diversifolia* Otto, *E. elata* Dehnh., *E. elata* Giordano, *E. translucens* A. Cunn., *E. Andreana* Naudin. with var. *nitida* Benth., *E. nitida* Hook. f., *E. radiata* Hook. f. (non Sieb.) var. 5, *E. ambigua* D. C. (?)].
2. *Eucalyptus linearis* Dehnhardt [synonym: *E. pulchella* Desf.].
3. *Eucalyptus Risdoni* Hook. f. [synonyms: *E. hypericifolia* R. Br. and Dum.-Cours., *E. amygdalina* Labill. var. *hypericifolia* Benth., *E. perfoliata* Dumont and others, *E. connata* Dum.-Cours. and Schauer with var. *elata* Benth., *E. radiata* Hook. f. (non Sieb.) partim.].

In the correspondence column of the *Chemist and Druggist*<sup>1)</sup> we find a note on eucalyptus oil by A. F. Collins, according to which the oil of *Eucalyptus globulus* does not possess a higher therapeutic value than the oils of *E. dumosa* and *E. oleosa*. The latter, and also oils of other species, are said to have been sold already for a long time as globulus oils at lower prices; Collins believes that not one fortieth part of the oils sold as globulus, are really obtained from that species.

**Fennel Oil.** The distillation of this oil was during the last season carried on by us on an exceptionally large scale, but it is open to doubt whether it will be the same this year, as in Galicia and Roumania high prices are expected. It is said that the results of the harvest have not been particularly good, but privately we have also heard opinions to the contrary. At the present moment it is impossible to say anything definite, and prices can only be fixed in two or three weeks' time.

**Oil of Field-balm.** The oil of field-balm, *Melissa calamintha* L. which was first<sup>2)</sup> distilled in our Bodenbach works in the year 1900, has again been produced there. The faintly yellow distillate possessing a peculiar pleasant aromatic odour, had the following constants:  $d_{15^\circ}$  0,8771.

<sup>1)</sup> *Chemist and Druggist* 67 (1905), 103.

<sup>2)</sup> Report April 1901, 59.

$n_D^{16} = 1.6057$ ;  $n_D^{20} = 1.49110$ ; acid number 0; ester number 8.3; ester number after acetylation 38.95; it makes no clear solution with 10 vol. 90 per cent. alcohol.

**Geranium Oil.** Since our last Report the prices of the Algerian distillate have dropped further to a considerable extent; they have now reached a level never known before, which will bring about a large demand for this article. This unexpected fall, of such extent as had been thought impossible, is no doubt to be attributed to the competition of the Réunion oil, which is now produced in quantities never dreamt of, and which is consigned to Europe without regard to the state of the market, the arrival of each large parcel causing a further depression in the value.

We must wait and see what the final result of this competition between the two French Colonies Algeria and Réunion will be; the present quotations of these two oils do not cover the cost of production.

The "Bulletin Commercial de l'île de la Réunion" published at Saint-Denis, writes on August 31<sup>st</sup> as follows on geranium oil:

This perfume is very scarce, the distillation has now ceased, and will only be recommenced in October. There are buyers at from fr. 23.25 to 23.50 per kilo in estagnons.

The export from 1<sup>st</sup> January to 30<sup>th</sup> September 1905 amounted to 36875 litres (against 25480 litres in the same period of 1904).

The consignments which arrived in the port of Marseilles between 1<sup>st</sup> Jan. and the end of August were:

Date	Steamer	Cases
17 <sup>th</sup> January	Melbourne	163
26 <sup>th</sup> "	Oxus	100
15 <sup>th</sup> February	Irraouaddy	186
25 <sup>th</sup> "	Natal	54
19 <sup>th</sup> March	Djemnah	82
28 <sup>th</sup> "	Melbourne	170
14 <sup>th</sup> April	Oxus	267
25 <sup>th</sup> "	Irraouaddy	115
10 <sup>th</sup> May	Ville de Majunga	56
15 <sup>th</sup> "	Natal	131
25 <sup>th</sup> "	Djemnah	133
15 <sup>th</sup> June	Melbourne	225
26 <sup>th</sup> "	Irraouaddy	90
16 <sup>th</sup> July	Natal	139
27 <sup>th</sup> "	Djemnah	107
15 <sup>th</sup> August	Melbourne	106
26 <sup>th</sup> "		77

Total 2203 cases of 12 1/2 kilos  
net = 27537 kilos,

and in addition to this, 2 casks and 47 bales (*fardeaux*), which latter have probably been erroneously included in these statistics. This quantity of say 28000 kilos within 8 months is enormous, and gives rise to the most serious apprehensions, as in our opinion it exceeds the requirements. In any case, the present low prices are not likely to improve in the near future. The perfumery trade ought to make abundant use of this state of affairs.

The low prices, which have ruled for the Indian product palmarosa oil, contribute towards the general depression. The first shipments of new oil are expected in the early part of December.

Since our scientific work has proved that the so-called gingergrass oil is not, as was formerly believed, an adulterated product, but represents a pure characteristic distillate, the interest in this article has grown in a marked degree. The stocks of this oil have gone down seriously, and offers of the new distillate are looked forward to with interest. Unfortunately, we have not yet succeeded in lifting the veil which covers the botanical origin of this oil, but we are diligently pursuing our efforts in this direction.

We have been able to observe interesting adulterations of geranium oil. From some samples submitted to us we could isolate benzoic acid which had probably been added to the oil in the form of ester, in order to cause an apparent increase in the content of geranyl tiglate in the oil. We are unfortunately unable to give details on the relative quantities which came under consideration, as the samples at our disposal were but small; we must therefore confine ourselves to the bald statement of the fact. The oils gave the following results on examination:

I.  $d_{15^{\circ}} 0,9074$ ;  $\alpha_D - 9^{\circ}$ ;  $n_{D20^{\circ}} 1,47196$ ; acid number 6,6; ester number  $74,8 = 31,5\%$  geranyl tiglate; ester number after acetylation  $222,64 = 73,5\%$  total geraniol; soluble in 1,8 and more volumes 70 per cent. alcohol; the dilute solution is opalescent; when left standing, a fairly large separation of paraffin occurs. The benzoic acid isolated melted at  $121^{\circ}$  to  $122^{\circ}$ .

II.  $d_{15^{\circ}} 0,9054$ ;  $\alpha_D - 8^{\circ} 8'$ ;  $n_{D20^{\circ}} 1,47313$ ; acid number 6,9; ester number  $61,3 = 25,8\%$  geranyl tiglate; soluble in about 2 and more volumes 70 per cent. alcohol.

Of palmarosa oil we received some samples which were suspected of adulteration owing to their abnormally high rotation; we were, however, unable to detect adulteration with absolute certainty. The properties of the oils may follow here briefly:

Oil I:  $d_{15^\circ}$  0,8917;  $n_D$  —  $7^\circ 30'$ ;  $n_{D20^\circ}$  1,47548; acid number 0,8; ester number 17,4; ester number after acetylation 242,2 = 81,4 % total geraniol; soluble in about 1,5 and more volumes 70 per cent. alcohol.

Oil II:  $d_{15^\circ}$  0,8940;  $n_D$  —  $5^\circ 55'$ ;  $n_{D20^\circ}$  1,47773; acid number 1,4; ester number 21,2; ester number after acetylation 242,5 = 81,5 % total geraniol; soluble in about 1,5 and more volumes 70 per cent. alcohol.

In the case of another sample which was found inferior owing to deficient solubility, we detected an adulteration with about 1,5 % fat or fatty oil, which of course also explains the bad solubility. For the rest the oil behaved as follows:  $d_{15^\circ}$  0,8925;  $n_D$  —  $0^\circ 40'$ ;  $n_{D20^\circ}$  1,47587; acid number 1,22; ester number 15,95; ester number after acetylation 256,92 = 87,52 % total geraniol; soluble in 1,5 and more volumes 70 per cent. alcohol; the dilute solution has a strong opalescence.

The results of our examinations of gingergrass oil mentioned in our Reports of April 1904, 56, October 1904, 44, and April 1905, 41, have meanwhile been published in a connected form in the *Journal für praktische Chemie* II, **71** (1905), 459.

**Oil of *Geum urbanum*.** E. Bourquelot and Hérissé<sup>1)</sup> have made further communications on the formation of the essential oil in *Geum urbanum* L., (common avens), which, according to the observations of the authors, is due to the decomposition of a glucoside.

The essential oil from the root of *Geum urbanum* had already been examined by Trommsdorff in 1818, and Buchner in 1844, but these authors were unable to decide with certainty whether the oil with the clove-like odour was identic with the eugenol from oil of cloves. Bourquelot and Hérissé obtained from 1 kilo roots 1 gm. oil, and by converting the latter into benzoyl eugenol, they established the fact that it consists chiefly of eugenol. In order to demonstrate that the eugenol is formed from a glucoside present in the root, by the action of a ferment, they proceeded in the following manner:

I. 150 gm. fresh roots of *Geum urbanum* were boiled with one litre 95 per cent. alcohol, and the alcoholic liquor filtered off was evaporated after a small quantity of calcium carbonate had been added. This extract only contained the glucoside whose presence in the root had been suspected, whilst the enzyme must have been destroyed by the boiling alcohol.

II. A portion of the fresh roots was then dried, pulverised, and submitted to exhaustive extraction in the cold with 90 per cent. alcohol,

<sup>1)</sup> Compt. rend. **140** (1905), 870; Journ. de Pharm. et de Chimie **21** (1905), 481; Comp. Report April **1904**, 59.

in order to remove the whole of the glucoside. As the enzymes are as a rule insoluble in strong alcohol, it was to be expected that the suspected enzyme had remained behind in the powdered root which had been separated from the alcohol and dried at 30°.

With the view of removing small traces of essential oil from the glucoside extract obtained from boiling alcohol, it was once more dissolved in alcohol, and again precipitated by the addition of ether, and separated off. The extract which was now completely odourless, dissolved in water, and developed the distinct odour of eugenol when the ferment-containing powdered root was added.

This reaction did not occur when the ferment-powder had been previously heated with water to 100°. Similarly, both the extract and the ferment-powder, each distilled by itself with water vapour, yielded a completely odourless distillate.

It may therefore be concluded from these experiments, that the root of *Geum urbanum* contains a glucoside, which is split up, with formation of eugenol, by an enzyme also present in the root. This agrees with the observation made, that the aqueous solution of the extract, which showed a feeble optical rotation, and reduced Fehling's solution, possessed this property in an increased degree after it had been mixed with the ferment-powder, which may be explained by the liberation of a sugar, probably glucose. As the various experiments with other ferments, such as emulsin, invertin, the ferments of *Aspergillus niger* v. Tgh. and also with other powdered plants, to produce the eugenol-odour in the extract-solution, did not succeed, the authors assume that the enzyme of *Geum urbanum* is a special ferment. This ferment was further only found in the root of the allied species *Geum rivale* L. (water avens). The ferment could not be separated from the root-powder, and was found to be completely insoluble in water. On the other hand, it was possible to isolate a small quantity of the glucoside from the alcoholic solution of the extract. It separated off slowly in the form of colourless crystals, when the alcoholic extract was carefully overlaid with ether. These crystals, dissolved in water, developed a powerful clove-odour when a small quantity of ferment-powder was added. For the new glucoside the name geïne is proposed, and for the enzyme the designation gease.

**Ginger Oil.** The only constituents of ginger oil known up to the present were the hydrocarbons camphene, phellandrene<sup>1)</sup> and zingiberene<sup>2)</sup>. We have recently also detected in the oil some oxygenated constituents which are not unimportant for the aroma of the oil, namely cineol, citral and borneol. The ginger oil examined,

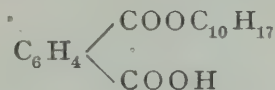
<sup>1)</sup> Bertram and Walbaum, Journ. f. prakt. Chemie. II. 49 (1894), 18.

<sup>2)</sup> v. Soden and Rojahn, Pharm. Zeitg. 45 (1900), 414.

which had been distilled by ourselves from African ginger, had the following constants:  $d_{15^\circ} 0,8853$ ;  $\alpha_D - 42^\circ 16'$ ;  $n_{D20^\circ} 1,49262$ ; saponification number 6,2; saponification number after acetylation  $42 = 9,8\%$  free alcohol of the formula  $C_{10}H_{18}O$ .

The oil distilled *in vacuo* at 5 mm. between  $40^\circ$  and  $125^\circ$ . From one of the first fractions, which distilled over at ordinary pressure between  $170^\circ$  and  $175^\circ$ , an abundant quantity of the iodol compound of cineol separated off when iodol was added. The compound, after washing with petroleum ether, melted at  $112^\circ$ ; when boiled with soda liquor, it split off an oil with the odour of cineol.

A fraction boiling between  $90^\circ$  and  $105^\circ$  at 5 mm. congealed, and yielded on collection crystals with the odour of borneol, which after recrystallisation from petroleum ether melted at  $204^\circ$ . Further quantities of borneol, and also a small quantity of an alcohol with a geraniol-like odour, could be obtained from the portion of the fraction which had remained liquid, by heating this portion with phthalic acid anhydride in benzene solution. The alcohols obtained from the phthalic ester acids by saponification with alcoholic potash, remained partly liquid; for this reason, another alcohol, possibly geraniol, must be present in addition to borneol. The free bornyl phthalic ester acid



melted, after recrystallisation from benzene and petroleum ether, at  $164^\circ$ . In the fractions from  $90^\circ$  to  $122^\circ$  at 5 mm. pressure, there was also found citral, which was separated off in the form of its solid bisulphite compound by shaking with sodium bisulphite liquor, and after decomposition with soda solution was converted into the citryl- $\beta$ -naphthochinonic acid melting at  $197^\circ$ .

**Gurjun balsam Oil.** Since the date of our last Report we received from a business friend a gurjun balsam which had been imported direct from the East Indies. The balsam was greenish blue and had a faint fluorescence, and with transmitted light a bright brown colour.  $d_{15^\circ} 0,9705$ ; acid number 7,65; ester number 0,9;  $n_{D20^\circ} 1,51532$ . On distillation with steam it yielded about  $60\%$  of a yellow oil with a balsamic odour;  $d_{15^\circ} 0,9236$ ;  $\alpha_D - 79^\circ 6'$ ;  $n_{D20^\circ} 1,50326$ ; ester number 0,99; soluble in about 9 and more volumes 95 per cent. alcohol.

**Hop Oil.** The reports on this year's hop harvest are throughout favourable. The total yield is decidedly in excess of the world's requirements, and a considerable drop in the prices of oil has taken place.

The results of the individual countries are estimated as follows:

Austria-Hungary . . . . .	about	370000	cwts.
Germany . . . . .	"	600000	"
Belgium and Holland . . . . .	"	120000	"
France . . . . .	"	75000	"
Russia . . . . .	"	95000	"
England . . . . .	"	600000	"
America . . . . .	"	440000	"

Total quantity about 2300000 cwts.,

against which the stocks at the breweries are said to be rather low. The world's annual consumption is estimated at about 2000000 to 2200000 cwts. Last year's crop amounted to 1650000 cwts.

Our quotations for hop oil have been considerably reduced.

**Jasmine "Schimmel & Co."** The increase in the sales of this excellent product proves that it is constantly more appreciated and more extensively used. It is employed not only as a substitute, but also for enriching the natural perfume from the blossom, and with the present taste for powerful concentrated compositions it renders in many cases invaluable services. We see here again a confirmation of the old experience, that the synthetic perfumes do not interfere with the natural ones, but that, on the contrary, they supplement each other, and both derive advantage from the progress of science which allows their use on a more comprehensive scale. As already mentioned before, the application of our jasmine is free from the risk that the manufactured articles become darker, or even acquire a red colour.

**Oil of *Lavandula Stoechas*.** The oil obtained by us from the dried blossoms of *Lavandula stoechas* L., in a yield of 0,755 % has a yellow-brown colour, and a strong camphor-like odour.  $d_{15^\circ}$  0,9620;  $a_D + 35^\circ 30'$ ;  $n_{D20^\circ}$  1,47909; acid number 5,16; ester number 13,1; soluble in 2 and more volumes 70 per cent. alcohol; the dilute solution is opalescent in consequence of a separation of paraffin. We succeeded in isolating dextrorotatory camphor from the oil (melting point  $175^\circ$  to  $175,5^\circ$ ); its oxime melted at  $117^\circ$  to  $118^\circ$ ,  $[\alpha]_D$  in alcoholic solution —  $41,6^\circ$ , semicarbazone, melting point  $231^\circ$ .

**Lavender Oil.** As already mentioned in our last Report, the conditions prevailing in the trade in this important article have forced us to make special arrangements for the supply of our requirements, and, by establishing works in a favourable situation, to provide also the opportunity of continuing and completing our scientific studies on lavender.

For the site of the works we selected Barrême in the department of the Basses-Alpes, which, situated at an altitude of 2300 feet, and



Schimmel & Co.'s distillery of lavender oil at Barrême (Basses-Alpes).  
(Rear)



surrounded by mountains over 3000 feet high, appears to possess all the qualifications necessary for the production of the finest lavender oils, rich in ester.

This factory is situated near the railway station, and is the first and only one in the place. It is fitted up with modern distilling plant, and has a fully equipped scientific laboratory which enables us to make the most thorough observations on the spot. The laboratory is under the superintendence of a chemist of our firm here, who has made a special study of lavender oil, and who was instructed to ascertain whether it would not be possible, by taking special steps during the distillation process, to produce oils of a still considerably higher ester-content than those at present met with in commerce. This problem has been solved at our Barrême works. The ester-content of the oils distilled this season, fluctuates between 47 and 52<sup>0</sup>/<sub>10</sub>, so that the average of the oils obtained by us is 50<sup>0</sup>/<sub>10</sub>.

This incontestable matter of fact is denied by the firm of Lautier Fils in Grasse, saying that oils of such a high natural ester-content did not exist. We do not doubt that such erroneous statement will be revoked as soon as the said firm will be set right by experience.

The quantities produced, amounting to only 3000 lbs., have been sold in the course of a few weeks.

This result would already be a sufficient justification for the establishment of our factory, and should be an inducement to others, to exchange their present primitive method of production for a better one. It is our intention to continue the study persistently, without needing the petty obstacles and difficulties which are put in our way.

Although at Barrême it is at most a question of the production of the above-said quantity of lavender oil, every opportunity is seized by French competitors to spread about the report that we are thus pushing up the prices.

In a circular recently issued, the aforesaid firm says that some of their competitors pretend them to be the cause of the great rise of the prices of lavender oil, and we hear that another important house in Grasse is charged with the same reproach.

As far as we are concerned, we immediately gave up buying when the market got excited and did our best to lower the exaggerated pretensions of the producers.

We have also taken up this distillation at Sault (Vaucluse), in an old factory which we have rented. With regard to the properties of the oil distilled by us, we would still mention that it does not show the same solubility as the ordinary distillate. For dissolving 1 volume oil, 5 to 7 volumes 70 per cent. alcohol are required. We are pleased to be able to submit to our readers two views of our Barrême factory, and would only point out, as an explanation of the view taken from

the rear, that the masses looking like hay, which are heaped up in front of the building, are lavender herb which has been distilled out.

With regard to adulterations of lavender oil, we are this time unable to report anything of importance. New adulterants have not been detected by us in our examinations, but we have repeatedly come across the usual ones, which we mentioned in our last Report<sup>1)</sup> in a tabulated form. Such an abundance of material as last time is not now at our disposal for the purpose of publication. But it is in any case more than sufficient to prove that the trade in adulterated oils is still diligently carried on. We confine ourselves to stating in the form of a table those data which are important for judging the oil, and for the rest would refer to our last Report. Oil No. 1 was adulterated with turpentine oil, Nos. 2 and 3 with rosemary oil, Nos. 4 and 5 with spike oil or Spanish lavender oil, and No. 6 consisted only of spike oil.

	$d_{15}^{\circ}$	$a_D$	Ester-content	Solubility in 70 per cent. alcohol
Lavender oil, pure	0,882 to 0,895	$-3^{\circ}$ to $-9^{\circ}$	30 to 40 <sup>0/10</sup> or more linalyl acetate	soluble in 2 to 3 or more vol., possibly slight opales- cence.
Adulterated lavender oils:				
No. 1.	0,8794	$+0^{\circ}42'$	13,2	insoluble
No. 2.	0,8919	$-0^{\circ}48'$	21,2	soluble in 3,5 vol.; when diluted strong opalescence.
No. 3.	0,8971	$+1^{\circ}11'$	15,4	soluble in 3 vol. with opal- escence, which disappeared when more solvent was added.
No. 4.	0,8986	$-4^{\circ}11'$	18,0	soluble in 3 and more vol.
No. 5.	0,8953	$-3^{\circ}12'$	22,8	soluble in 2 to 2,5 and more vol. with very faint opales- cence.
No. 6.	0,9100	$+0^{\circ}30'$	4	soluble in 2,5 and more vol.

**Lemongrass Oil.** The prices during the last six months have remained without change, as the moderate supplies were always readily taken up by the current demand. From the 1<sup>st</sup> Jan. to 30<sup>th</sup> June of this year shipments amounted to:

78 cases to London  
45 „ „ Marseilles  
52 „ „ Hamburg  
40 „ „ New York  
326 „ „ ports in Asia (Bombay, etc.)

total 541 cases,

<sup>1)</sup> Report April 1905, 52.

whilst the total shipments during the last season, i. e. from 1<sup>st</sup> July 1904 to 30<sup>th</sup> June 1905, show the following figures:

246 $\frac{1}{2}$	cases to London
76	„ „ Havre
375	„ „ Marseilles
21	„ „ Antwerp
252	„ „ Hamburg
115	„ „ New York
797	„ „ ports in Asia (Bombay, etc.)
total 1882 $\frac{1}{2}$ cases,	
against 2222 $\frac{1}{2}$ cases in 1903—1904	
and 2806 „ „ 1902—1903.	

In view of these statistics, it is probable that cheaper prices cannot be reckoned upon in the near future.

In the Ceylon Administration Reports of the Royal Botanical Garden for 1904, the following interesting paragraph appears on the cultivation and distillation-experiments with lemongrass plants:

In 1902, Mr. Bowman sent me cuttings which have taken on, and an area of more than an acre has been planted with this species. A small sample has been distilled here, and although 700 lbs. fresh grass only yielded 1 lb. oil, I mention this as being the first result obtained here. The field of 2 acres, planted in July 1904, was cut in December, and produced 12126 lbs. fresh grass, from which 26 $\frac{1}{2}$  lbs. oil were distilled.

The practical realisation of the cultivation of this plant on a reasonable scale in Ceylon is highly desirable, as the present production is insufficient, and the manufacture of citral from lemongrass oil is capable of great expansion, if only sufficient quantities of raw material could be had at moderate prices.

The high prices paid during the last 18 months for lemongrass oil, have greatly stimulated the interest in the cultivation of lemongrass in Ceylon, as we learn from a paper read by Herbert Wright<sup>1)</sup> before the Agricultural Society of Ceylon. In the South of Ceylon, where the oil industry is already carried on, and where lemongrass grows well, further quantities have been planted out. According to experience gained by Wright during three years at Peradeniya, lemongrass gives the same yield of oil at altitudes of 2000 feet in the Central provinces, as at low levels in the South and South West provinces. Whilst in previous years the cultivation of lemongrass has been neglected, as that of citronella grass promised greater profit, the former would at the present prices of the oil probably be very remunerative.

<sup>1)</sup> Chemist and Druggist **67** (1905), 17.

The fact, that the prices of lemongrass oil are now four times as high as five years ago, has induced the principal consumers, the citral and ionone industry, to look for other sources of citral. Such a source is said to be found in the oil of *Backhousia citriodora* F. v. Müll. The plant is reported to grow in large quantities in Queensland, on the coast between Brisbane and Gympie. As in that district no oil industry exists as yet, it has not yet been possible to place this oil on the market in large quantities. It is 10 to 20% richer in citral than lemongrass oil, and if it can be shipped regularly, it may become an important article of commerce, the more so, as the probability of consumption increases with the high prices of lemongrass oil.

It is of course well known that citral has also been detected in this oil in our laboratory, as long ago as 1888<sup>1)</sup>.

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Of lemongrass oil, which on the whole is rarely adulterated, we received two samples for approval which both behaved abnormally, and were more or less adulterated with cocoa butter. This was proved by the determination of the melting point and the saponification number of the residue remaining behind when the oils were submitted to steam distillation. The results of the examinations were as follows:

Oil I:  $d_{15^\circ}$  0,9059;  $n_D$  —  $3^\circ 40'$ ; aldehyde-content about 61%; insoluble in 10 volumes 70 per cent. alcohol; soluble in 1,0 volume 80 per cent. alcohol, when 1,5 or more volumes were added, cloudiness occurred and oil separated off; non-volatile with water vapour were about 15% fat of the melting point  $27^\circ$  and saponification number 255,4.

Oil II:  $d_{15^\circ}$  0,9043;  $n_D$  —  $2^\circ 52'$ ; aldehyde-content about 64%; not soluble in 10 volumes 70 per cent. alcohol; soluble in 0,8 vol. 80 per cent. alcohol, when 1,5 and more vol. were added cloudiness occurred. Residue on steam distillation about 10,7% fat of the melting point  $26^\circ$ .

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Some considerable time ago Doebner<sup>2)</sup> suspected the presence in lemongrass oil of small quantities of an aldehyde isomeric with citral, on the strength of the composition of a compound melting above  $225^\circ$ , isomeric with citryl- $\beta$ -naphthocinchonic acid. We have now succeeded in giving a clearer proof of the presence of a second aldehyde of the formula  $C_{10}H_{16}O$  in lemongrass oil. When working up 2000 kilos lemongrass oil into citral, the fraction (about 400 gm.) regenerated from the bisulphite compound, boiling between methyl heptenone and citral, was repeatedly carefully fractionated, and by

<sup>1)</sup> Comp. Report 1888, 20 and April 1905, 83.

<sup>2)</sup> Berliner Berichte 31 (1898), 1891.

these means a fraction of the boiling point  $70^{\circ}$  to  $80^{\circ}$  (6 mm. pressure) was obtained, which was free from methyl heptenone and citral, but did not yet appear to be uniform. For a further separation the most suitable process proved to be the treatment of the single fractions with 3 parts 40 per cent. sodium bisulphite liquor. It was then found that the lower-boiling fractions dissolved almost without separating off an insoluble bisulphite compound, whilst the higher boiling portions separated off perceptible quantities of a slimy bisulphite compound, from which the rest was filtered off. From the filtrate a substance boiling at  $72^{\circ}$  to  $76^{\circ}$  (7 mm. pressure) was regenerated with soda, which was possibly not yet entirely uniform. By repeated fractionating there was obtained a fraction ( $d_{15}^{\circ}$  0,9081;  $n_{D20}^{\circ}$  1,45641;  $n_D + 0^{\circ}$  50') boiling constantly at  $68^{\circ}$  (6 mm. pressure) and yielding readily a semicarbazone, which after repeated recrystallisation from methyl alcohol melted at  $188^{\circ}$  to  $189^{\circ}$ :

0,1252 gm. of the subst.: 0,2890 gm.  $CO_2$ , 0,1044 gm.  $H_2O$ .

Found:		Calculated for $C_{11}H_{19}ON_3$ :
C	62,9 %	63,1 %
H	9,26 %	9,1 %

According to this, the semicarbazone of the melting point  $188^{\circ}$  to  $189^{\circ}$  originates from a compound  $C_{10}H_{16}O$ . The proof that it was here a question of an alcohol and not a ketone, was readily supplied by oxidation with moist silver oxide into a liquid acid  $C_{10}H_{16}O_2$  of the boiling point  $130^{\circ}$  (9 mm. pressure), whose silver salt dissolves with difficulty in water, and can be readily recrystallised from alcohol.

Determination of silver: 0,3298 gm. salt yielded 0,1304 gm. Ag.

Found:	Calculated for $C_{10}H_{15}O_2Ag$ :
39,54 % Ag.	39,27 % Ag.

From the above-mentioned insoluble bisulphite compound, the n-decylic aldehyde (4 gm.), boiling point  $80^{\circ}$  to  $81^{\circ}$  (6,5 mm. pressure),  $d_{15}^{\circ}$  0,8361, which we have already detected in numerous essential oils, was regenerated, and was identified by its semicarbazone of the melting point  $102^{\circ}$ , and by oxidation into n-capric acid, melting point  $31^{\circ}$ .

In answer to a request expressed by its readers, the *Journal d'Agriculture tropicale*<sup>1)</sup> publishes a treatise on citronella and lemon-grass oils, which does not contain much that is new to us, but yet gives some remarks by experts which are worth quoting.

For example, we find there with regard to the state of the cultivation and oil industry in Java, from letters by the French vice-consul at Batavia, M. Paul Serre, that of the andropogon grasses chiefly

<sup>1)</sup> Journal d'agriculture tropicale 5 (1905), 42.

lemongrass and citronella thrive and are cultivated, whilst vetiver is neglected because it thrives specially in marshy, unhealthy districts. Plants suitable for cultivation in Java are further basil, peppermint, balm, and others. Lemongrass oil is manufactured chiefly in three places in Java (Tjitjourouk, Kediri, Tjiaoui); about 300 kilos lemongrass yield 1 kilo essential oil. In order to make this industry specially remunerative, the investment of a large capital is essential; the writer of the letter believes that the most profitable way will be to manufacture the oil in the country itself into various perfumes for the East Indian market. The principal centre for the trade in lemongrass oil is Cochin, which has exported from 1893 to 1903, 28000 to 40,000 bottles of about 620 gm. annually.

It had been easy to introduce into commerce the Java citronella oil, against Ceylon citronella oil which often come on the market adulterated by middlemen, and it readily became a great favourite on account of its excellent qualities and purity. The manufacturers of better-class soaps became the principal consumers. How important a part citronella oil plays in commerce is shown by the fact that Ceylon in the year 1899 produced 1 $\frac{1}{2}$  million pounds.

With regard to the information communicated according to Sawyer, we have already referred to this matter in our last Reports<sup>1)</sup>.

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In the Report of the Department of Agriculture, Mysore, we find in addition to information on experimental cultivations and examinations of the soil, fertilizers, water, and coffee, also some particulars by A. Lehmann<sup>2)</sup> on "grass oil". Of the three samples examined, one originated from Sulekere, where the oil is distilled as a commercial article, and two from Nilgiris where this oil industry has not yet become firmly established. Only the last two oils had a distinct citral odour. As probably neither of them were pure oils, we will refrain from giving further details.

**Linaloe Oil.** The supplies of Mexican oil have lately been sufficient for the demand but without allowing the accumulation of large stocks. As a consequence, the prices could be maintained at the same level as hitherto. On the other hand, it is said that of the Cayenne distillate important parcels have been heaping up, which cannot be realised without exerting a heavy pressure on the value. For this reason it is not impossible that this kind of oil may on occasion be purchased at a decidedly lower figure.

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<sup>1)</sup> Report October 1904, 53, and April 1905, 55.

<sup>2)</sup> Fourth annual Report of the Agricultural Chemist for the year 1902/03, Bangalore, 1904.

In our Report of October 1904, p. 56, we for the first time published information on absolutely normal dextrorotatory linaloe oil. The property of dextrorotation, which had until that time been unknown for this oil, has recently been repeatedly observed by us, and that with oils from different sources.

We give below some details on their examination:

Oil I:  $d_{15}^{\circ}$  0,8816;  $\alpha_D + 6^{\circ} 3'$ ; acid number 1,7; ester number 20,0;  $n_{D20}^{\circ}$  1,46209; soluble in 1,6 and more volumes 70 per cent. alcohol. On distillation *in vacuo* there passed over:

	Pressure	Temperature	%	Optical rotation	Remarks
1.	4 mm.	up to $66^{\circ}$	8,5	$\alpha_D + 6^{\circ} 30'$	} linalool fraction
2.	4 "	$66^{\circ}$ to $67,5^{\circ}$	23,5	$\alpha_D + 8^{\circ} 18'$	
3.	4 "	$67,5^{\circ}$ to $68^{\circ}$	32,1	$\alpha_D + 9^{\circ}$	
4.	5 "	$73^{\circ}$ to $76^{\circ}$	17,0	$\alpha_D + 7^{\circ} 30'$	
5.	5 "	$76^{\circ}$ to $82^{\circ}$	2,1	$\alpha_D + 3^{\circ} 20'$	
6.	5 "	$82^{\circ}$ to $96^{\circ}$	8,7	$\alpha_D - 10^{\circ} 5'$	

Oil II:  $d_{15}^{\circ}$  0,8783;  $\alpha_D + 8^{\circ}$ ; acid number 1,4; ester number 3,5;  $n_{D20}^{\circ}$  1,46149; soluble in 2,0 and more volumes 70 per cent. alcohol. On distillation *in vacuo* the following passed over:

	Pressure	Temperature	%	Optical rotation	Remarks
1.	10 mm.	$60^{\circ}$ to $86^{\circ}$	4,5	$\alpha_D + 5^{\circ} 24'$	} linalool fraction
2.	10 "	$86^{\circ}$ to $90^{\circ}$	9,0	$\alpha_D + 8^{\circ} 50'$	
3.	10 "	$90^{\circ}$ to $91^{\circ}$	15,0	$\alpha_D + 11^{\circ} 21'$	
4.	14 "	$95^{\circ}$ to $97^{\circ}$	51,0	$\alpha_D + 11^{\circ} 15'$	
5.	14 "	$97^{\circ}$ to $100^{\circ}$	5,0	$\alpha_D + 8^{\circ}$	
6.	14 "	$100^{\circ}$ to $110^{\circ}$	3,0	$\alpha_D - 11^{\circ}$	
7.	14 "	$110^{\circ}$ to $120^{\circ}$	3,0	$\alpha_D - 18^{\circ} 20'$	

Oil III:  $d_{15}^{\circ}$  0,8801;  $\alpha_D + 2^{\circ} 54'$ ; acid number 1,3; ester number 3,74; soluble in 1,6 and more vol. 70 per cent. alcohol.

The further chemical examination of the oil mentioned sub I, which only dealt with the alcohol contained in the oil, proved that the dextrorotatory linaloe oil — apart from the optical rotation — has the same constituents which are important for the odour, as laevorotatory linaloe oil. The percentages of the composition are also probably the same for both oils. Besides two terpenes which are of no consequence for the odour of the oil, and one sesquiterpene<sup>1)</sup>, the

<sup>1)</sup> Barbier and Bouveault, Compt. rend. **121** (1895), 168.

following are present in laevorotatory linaloe oil: l-linalool<sup>1)</sup>, geraniol<sup>2)</sup>, methyl heptenone<sup>3)</sup>, and d-terpineol<sup>4)</sup> of the melting point 35° ( $\Delta_1$ -terpene-8-ol).

For the d-linalool isolated from the above-mentioned dextrorotatory oil, which has been included in our price lists, we ascertained the following physical constants:  $d_{15^\circ}$  0,8723;  $\alpha_D + 9^\circ 2'$ ;  $n_{D20^\circ}$  1,46229; soluble in 10 volumes 50 per cent. and 4 volumes 60 per cent. alcohol.

A particularly interesting observation is this, that in the dextrorotatory linaloe oil, l-terpineol of the melting point 35° is present. The proof of this was found in a fraction forming the last runnings of the saponified oil, and which had the specific gravity 0,9090 and the optical rotation  $-11^\circ 20'$ . By means of repeated fractionating we isolated from it a viscid oil with an odour like terpeneol, which became solid after inoculation with a terpeneol crystal ( $\Delta_1$ -terpene-8-ol). The physical constants of the compound purified by crystallisation were: boiling point 85° (3 to 4 mm. pressure); 219° to 221° (ordinary pressure); melting point 34° to 35°;  $\alpha_D - 27^\circ 20'$  (determined in the molten state);  $n_{D20^\circ}$  1,48131. By combination with phenyl isocyanate the terpeneol yielded a phenyl urethane of the melting point 112°.

For the isolation of the geraniol a fraction served of the following constants: boiling point 98° to 105° (5 mm. pressure);  $d_{15^\circ}$  0,8910;  $\alpha_D - 2^\circ 53'$ . The separation took place in the usual manner with phthalic acid anhydride. The alcohol mixture separated from the sodium-salt solution of the phthalic ester acid by saponification, was further submitted to treatment with pulverised calcium chloride for the purpose of producing the geraniol in the pure state. From the solid purified calcium compound the pure geraniol was separated off by water.

We observed the following constants: boiling point 92° (3 mm. pressure);  $d_{15^\circ}$  0,8803;  $\alpha_D \pm 0^\circ$ ;  $n_{D20^\circ}$  1,47678. The diphenyl urethane produced from it melted readily at 82°.

The inactive oil of the boiling point 225° to 228°, which after having been treated twice no longer reacted with calcium chloride, scarcely differed in the odour from geraniol. But it reacted with diphenyl carbamin chloride and pyridin, with formation of a compound which in the crude state melted at 61° to 64. By means of fractional crystallisation from dilute methyl alcohol a well-crystallised body could be separated off from this compound, which melted readily at 51° to 53°, and which therefor corresponds with the diphenyl

<sup>1)</sup> Morin, Compt. rend. **92** (1881), 998, and **94** (1882), 733; Ann. de Chim. et Phys. V. **25** (1882), 427; Semmler, Berl. Berichte **24** (1891), 207.

<sup>2)</sup> Report April **1892**, 24; Report October **1894**, 35; Report October **1900**, 43.

<sup>3)</sup> Report October **1894**, 35.

<sup>4)</sup> Report October **1900**, 43.

urethane which v. Soden and Treff<sup>1)</sup> have obtained from the alcohol designated as nerol. We have no doubt that in the ordinary laevorotatory linaloe oil, a fraction of the same properties will also be found.

**Mustard Oil, from seed.** A large parcel of Indian mustard seed has just been worked up, but at the current depressed prices it gives only the barest possible profit.

The fatty mustard oil, obtained as a by-product, is readily sold at good prices. This belongs to the non-drying oils, and for this reason is used for the lubrication of fast-running machinery.

The application of the fatty oil for cosmetics has also lately been pushed. In Russia (Sarepta), where it is obtained in large quantity, it is used for kitchen purposes.

The determination of the essential oil in the mustard seed, published by C. Hartwich and A. Vuillemin<sup>2)</sup>, has already been mentioned in our Report<sup>3)</sup> of October 1904. We would, however, again call special attention to the work of the above authors, as it contains a summary of the methods hitherto in use for the quantitative determination of mustard oil.

According to the examinations made by the authors, the content of mustard oil in *Brassica nigra* Koch. fluctuates between 0,825 and 0,911%. Whereas the German Pharmacopoeia requires a content of at least 0,55%, Hartwich and Vuillemin are of opinion that for a drug which must consist exclusively of *Brassica nigra* Koch., a content of 0,8% should unhesitatingly be required.

**Neroli Oil.** It is generally known that this year's harvest of orange blossoms in the department of the Alpes-Maritimes has given very unfavourable results owing to severe damage by frost and continuous rain during the harvesting period, and in conjunction with the steps taken by the Société coopérative, the prices of the blossoms have gradually been advanced up to about 1 franc.

Owing to this, the fine qualities of neroli oil have now reached enormously high prices, which have to be paid whether it is liked or not.

According to the information published in the *Journal de Vallauris* of May 27<sup>th</sup> of this year, the installations of the above-named Société.

<sup>1)</sup> v. Soden and Treff, *Chemiker-Zeitung* **27** (1903), 897; Report April 1904, 108; further Hesse and Zeitschel, *Journ. f. prakt. Chem.* II. **66** (1902), 481; Report April 1903, 53; v. Soden and Zeitschel, *Berl. Berichte* **36** (1903), 265; Report April 1903, 54; v. Soden and Treff, *Berl. Berichte* **37** (1904), 1094; Report October 1904, 79.

<sup>2)</sup> *Apotheker-Zeitung* **20** (1905), 199.

<sup>3)</sup> Report October 1904, 59.

in which at that time already 1250 persons were interested, were completely ready at the commencement of the season. With regard to the quantity of blossoms worked up by the Société, further details are wanting, and the same applies to the progress of the quarrel with the Grasse manufacturers. Our informant estimates the crop of blossoms this year at 900000 kilos, of which about 700000 kilos are said to be in possession of the Société coopérative. In normal years the blossom-production amounts to more than double the above quantity.

From one of our business friends in the South of France we have received a number of orange blossom oils, which were made up according to the time of production. We have observed there a certain regularity in the alteration of the constants, as will be seen from the following table.

$\frac{c}{N}$	Distillate of	$d_{15^{\circ}}$	$\alpha_D$	$n_{D20^{\circ}}$	Ester number	Solubility
1	11 May to 25 May	0,8764	+ 2° 37'	1,47303	46,5	Soluble in 1,2 and more vol. 80% alcohol; separation of paraffin decreases from No. 1 to No. 4.
2	26 May to 30 May	0,8762	+ 4°	1,47245	44,0	
3	31 May to 2 June	0,8745	+ 5° 2'	1,47264	37,1	
4	3 June to 7 June	0,8741	+ 5° 30'	1,47186	38,1	

Whilst therefore during the present year as time advanced a gradual drop in the specific gravity and the ester number, and also an increase in the rotatory power could be observed, no such regular process could be discovered in previous years<sup>1)</sup>.

**Nutmeg Oil.** The waste nuts which are used for the distillation remain unaffected by any movements of the market, and a sufficient supply was available to execute in full the exceptionally heavy export orders.

**Orris Oil.** In continuation of the information on the orris root market contained in our April Report, our correspondents describe the present situation as follows:

According to our previous information the quantity at disposal at the end of February 1905 amounted to . . . . .	about 840 tons
Deduct from this the shipments from the beginning of March to the end of August 1905 . . . . .	„ 280 „
Leaves at disposal on Sept. 1. 1905 . . . . .	about 560 tons
The total quantity shipped in 12 months	
Sept. 1904/August 1905 amounted to . . . . .	„ 500 tons
against	
Sept. 1903/August 1904 . . . . .	„ 820 „
Sept. 1902/August 1903 . . . . .	„ 840 „

<sup>1)</sup> Comp. Reports October 1901, 38, October 1902, 53, October 1903, 49, October 1904, 63.

The preceding figures, as compared with a previous annual average quantity shipped of about 900 tons, appear to confirm the information which has repeatedly reached us, viz., that especially in France, large stocks of roots and their products have in the course of time been gradually accumulating. Whether this is perhaps connected with a decrease in the consumption, is a matter on which we are unable to express an opinion; it would seem more probable that the extremely cheap prices could only stimulate the consumption of this article and of its products which are so valuable for the perfumery industry.

Judging from the roots harvested up to the present, the quantity of which we estimate at fully 300 tons, the quality of the new crop promises on the whole to turn out somewhat better than that of the previous year. With regard to the quantitative total results, nothing can as yet be definitely stated, for, according to previous experience, good or low selling prices during the harvest time, which may possibly last into November, usually exert either an upward or a downward influence on the quantity gathered. Ripe for gathering are the extensive plantings of 1902, and those of 1903 which are about one tenth less. The latter may, but the former must be gathered this autumn. If we were asked to name the probable figures of the harvest, our estimate would be about 700 tons. In such case, the total quantity at disposal for the season Sept. 1905/August 1906 would come to (as above) . about 560 tons  
plus result of harvest „ 700 „

against

total about 1260 tons

Sept. 1904/August 1905 . . . . .	about 1160 tons
Sept. 1903/August 1904 . . . . .	„ 1310 „
Sept. 1902/August 1903 . . . . .	„ 1400 „

The foregoing appears to make it clear that the producers cannot for a long time to come expect a return of the former golden times. Many a producer nursed this article during the favourable period for many years as a pet child which in the present bad times he is unable to abandon altogether. For this reason the quantities planted out were reduced at a slower rate than the ruinous selling prices would otherwise have demanded. But the latter can hardly improve permanently, so long as the stocks so enormously exceed the requirements. For the new crop assorted roots, the parity of 36/37 marks cif. Hamburg is now paid. During the last twelve months the fluctuations in the price were again unimportant; the prices paid were 36/38 marks cif. Hamburg for assorted roots, and 32/34 marks for seconds. The last-named quality was difficult to obtain in recent times, as last year's harvest yielded almost throughout inferior qualities which were not suitable for picking (which leaves the seconds), and which were therefore used untouched as assorted roots. When the present crop is stored, seconds may possibly again be more readily obtainable.

We would still mention here that in the Veronese producing district the results of the last harvests show a very considerable falling-off. Only a few years ago the annual production there came up to 600 tons, but last year it was not more than about 120 tons, and this year our correspondents reckon on about 80 tons. Sugar-beet has displaced the Veronese orris cultivation, and is said to be highly remunerative. For the rest, such large stocks of orris roots had been held over in the Veronese district from the previous rich years, that the small result of the last harvest found absolutely no expression in the value of the article; on the contrary, the prices there continued to fall away, and to-day they are still, for example for the so-called "mercantile Veronese quality", at the lowest never before known level of about 22 marks cif. Hamburg, an article which 10 years ago was paid with 80 marks. It is used by preference in the United States, and if later on a proper demand for it at last arises, the price will no doubt improve.

The foregoing shows sufficiently that in future also the extraordinary favourable quotations of orris oil can be reckoned upon.

**Patchouli Oil.** The over-production of patchouli leaves has had such an important influence on the value, that the quotations of the oil have now again come within reach of the lowest level.

The statistics of the last 10 years show the following: —

value on October	1 <sup>st</sup> 1896	54 marks per kilo			
" "	" 1 <sup>st</sup> 1897	56	"	"	"
" "	" 1 <sup>st</sup> 1898	36	"	"	"
" "	" 1 <sup>st</sup> 1899	30	"	"	"
" "	" 1 <sup>st</sup> 1900	30	"	"	"
" "	" 1 <sup>st</sup> 1901	27	"	"	"
" "	" 1 <sup>st</sup> 1902	38	"	"	"
" "	" 1 <sup>st</sup> 1903	45	"	"	"
" "	" 1 <sup>st</sup> 1904	45	"	"	"
" "	" 1 <sup>st</sup> 1905	36	"	"	"

According to information from Penang and the Straits, the plantations have meanwhile been greatly reduced, as the present prices are no longer remunerative. We believe that advantage should be taken of the present weak position, to make abundant purchases of patchouli oil.

J. Rodie<sup>1)</sup> points to the difficulties met with in valuing the patchouli oils of commerce; he further calls attention to the fact, that patchouli oil in the course of time undergoes a fairly considerable change in its properties, and becomes more valuable for purposes of perfumery, as the odour improves, and the solubility in 80 per cent. alcohol increases. He was able to observe these changes in 3 different absolutely pure oils, of which one was 11 and one 6 years old, and the third dated from the year 1904. For the rest J. Rodie confirms the results obtained by us<sup>2)</sup> in the examination of a patchouli oil of our own distillation.

**Peppermint Oil, American.** As in previous years, our New York firm, which keeps a permanent representative in the peppermint districts to look after its interests, has again in the course of this summer had a detailed inspection made of the whole of the producing districts, and has provided us with the following report on the situation of this article: —

<sup>1)</sup> Chem. Zeitg. Repert. 29 (1905), 92.

<sup>2)</sup> Report April 1904, 68.

## I. Wayne County (New York).

In consequence of the high prices obtained for peppermint oil in the season of 1904, a large number of farmers has been induced to plant out large quantities, in order to profit still as much as possible from the state of the market, and so it has come about that the area cultivated this year with peppermint is fully half as large again as last year. Even those who, disheartened by the low level of prices reached some years ago, had abandoned the cultivation, have taken it up afresh. As already mentioned in our October Report of last year, the high price then ruling for peppermint roots induced many farmers to devote a large portion of their plantations to the production of such roots. Our prediction, that in consequence of this an increased cultivation of peppermint would have to be reckoned upon in 1905, has come true, and the fact that this year scarcely half the price of last year was asked for roots, shows sufficiently that there was no lack of material for planting out. A not unimportant part of the cultivations in Wayne County has suffered much from rain; other tracts have been much exposed to the severity of the winter, and are overgrown with weeds. In addition to this, a bug-like insect called "grub" has again made its appearance, and is reported to have done a good deal of damage in some districts. At the time of the last inspection-journey, about two weeks ago, the distillation had commenced only at a few places, so that no clear idea could yet be formed on the yield of oil.

The area cultivated with peppermint is distributed this year as follows over the various districts:

Marion . . . . .	94 $\frac{1}{2}$	acres
Sodus . . . . .	105	"
Lyons . . . . .	174 $\frac{3}{4}$	"
Rose . . . . .	44	"
Galen . . . . .	33	"
Junius . . . . .	34 $\frac{1}{2}$	"
Phelps . . . . .	52	"
Phelps (Hopewell Centre)	25	"
Williamson . . . . .	16 $\frac{1}{4}$	"
E. Palmyra . . . . .	115 $\frac{1}{2}$	"
Arcadia . . . . .	140 $\frac{1}{4}$	"
Arcadia (West of Fairville)	43 $\frac{1}{2}$	"
Arcadia (West of Zurich)	43 $\frac{3}{4}$	"
Arcadia (East of Newark)	11	"

Total 933 acres.

The stocks of old oil still in the hands of producers are said not to exceed 3000 lbs.

At one time Lyons was the most important place for the peppermint oil trade in Wayne County, but lately Newark must be regarded as the centre. With respect to the production, the above summary shows that the Arcadia district occupies the first place, and is only approached by Lyons, whilst the other districts of the peppermint oil production only comprise comparatively small tracts which are distributed over the whole County.

The opinion is now rightly held that it will depend entirely upon the prices which will be obtained this season, whether or not the farmers will increase their plantations for next year.

## II. Michigan and Indiana.

In Michigan the weather conditions during the spring and early summer were on the whole not particularly favourable for the development of the plants. The lower-lying fields were too damp to allow of the planting out in all places, and as a consequence the extent of the cultivation did not come up to expectations. Especially in the North Western part of the State, cloud-bursts caused a considerable amount of further damage, and the subsequent heat was so favourable for the development of weeds, that a large number of fields suffered greatly from it. On the other hand, the plantations in the districts situated at a higher level are in excellent condition, and promise an extremely satisfactory result. The area of the individual districts, which, as is well known, far exceeds that of the State of New York, is as follows:

County of Muskegon . . . .	about 800 acres
„ „ Allegan . . . .	„ 2000 „
„ „ Van Buren . . . .	„ 1900 „
„ „ Cass . . . .	„ 175 „
„ „ Berrien . . . .	„ 600 „
„ „ St. Joseph . . . .	„ 1200 „
„ „ Branch . . . .	„ 200 „
„ „ Kalamazoo . . . .	„ 500 „

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Total, about 7375 acres.

The probable yield of oil is estimated at about 25 lbs. per acre.

The cultivation in Indiana amounts in all, in the districts of South Bend, Mishawaka and Osceola, to about 1000 acres, which means an increase up to about double the area of last year. On an average, the fields are here in a better condition than in 1904, and it is believed that an oil yield of about 35 lbs. per acre may be reckoned upon.

With regard to the above information, the probable result of the whole peppermint harvest may therefore be calculated as follows, assuming that in Wayne County an average quantity of 25 lbs. per acre is also attained:

Wayne County . . . . .	about 933 acres,	about 23 325 lbs.
Michigan . . . . .	7375 „ „	184 375 „
Indiana . . . . .	1000 „ „	25 000 „
		Total about 232 700 lbs.

This total result is sufficiently large to have a decided effect on the prices, and in any case will prevent a repetition of the “booms” of the last two years. Attempts will no doubt be made from time to time to instil some life in this article, but people will hardly lend themselves to supporting a bullish movement. The low value of the Japanese oil is also against such a movement.

Crude American peppermint oil reached its highest price of 5 dollars per lb. in October 1902, and maintained this level by all sorts of machinations until February 1903. From that time the prices went uninterruptedly back, and at this moment they have arrived at about \$ 2.50. It appears to us out of the question that they will ever return to the level of 1901; on the contrary, we consider the present quotation as normal, and suitable for laying in abundant supplies. Our quotations of the two brands of our New York firm are regulated according to the present market value of first quality oil.

**Peppermint Oil, Japanese.** According to the reports received by us a few weeks ago from our friends in Japan, the peppermint harvest now taking place affords the following picture:

Producing District	1904	1905	1905	1905
	Area under cultivation	Probable area under cultivation	Probable crop of dried leaves	Probable quantity of peppermint oil produced
Yamagata Ken	715,5 cho <sup>1)</sup>	No great difference as compared with last year	450 000 kwan <sup>1)</sup>	28 000 kin <sup>1)</sup>
Akita Ken	No peppermint plants grown	—	—	—
Okayama Ken	1391,5 cho	1400,0 cho	1 370 000 „	117 000 „
Kochi Ken	26,8 „	10,0 „	19 060 „	771 „
Kagoshima Ken	No peppermint plants grown	—	—	—
Hiroshima Ken	1275,8 cho	801,5 „	847 567 „	137 173 „
Hokkaido	1164,7 „	1252,0 „	1 282 936 „	75 647 „
	4574,3 cho	4179,0 cho	Total result	358 591 kin

<sup>1)</sup> 1 cho = 2,446 acres; 1 kwan = 7,88 lbs.; 1 kin = 1,33 lbs.

or about 474 000 lbs. With regard to the information concerning the area cultivated, this stands as follows:

decrease in two districts . . . . .	491,1 cho
increase in two districts . . . . .	95,8 „
decrease in 1905 . . . . .	395,3 cho

or about 9% as compared with 1904. These statistics are said to be reliable.

Great efforts are made in Japan to raise the value; in the first place, offers for prompt delivery are held back, and for later deliveries high prices are asked. The fact chiefly relied upon is this, that the first crop in Bingu-Bitchin has turned out smaller than had been accepted, — but the first crop is no criterion of the total harvest. The decisive factors are the second cut in September, and the third in November. Furthermore, the Japanese do not take into consideration that at the low prices a heavy speculation has taken place in this article in Europe and America, and that important speculative stocks are held in London, Hamburg, and here, which will have the effect of checking the proposed advance in the prices. The decline in the American peppermint oil acts in the same manner, and for these reasons any upward movement in the value of Japanese oil would probably be only of a temporary character, and not permanent. In the opinion of our friends, it will be impossible to determine the prices before November.

The shipments of liquid peppermint oil and menthol crystals from Japan during the first 6 months of this year, show the following figures:

	from Yokohama	from Kobe	total
January	548 cases	258 cases	806 cases
February	646 „	194 „	840 „
March	678 „	494 „	1172 „
April	189 „	186 „	375 „
May	236 „	74 „	410 „
June	91 „	109 „	200 „
	2488 cases	1315 cases	3803 cases

Taking the case at 60 lbs., the total export during the first six months of 1905 comes to

228 180 lbs.,

a quantity which has never been reached before in a similar period, and which confirms our opinion that heavy stocks must still exist in Europe, and probably also in America. According to the Hamburg statistics, the imports from Japan in 1904, partly direct, and partly via China, amounted to

59870 kilos, value 737530 marks,

that is to say, to more than half of Japan's entire annual output. This shows that Germany is nowadays the most important customer of Japan. The above figures include our own very considerable importation.

**Peppermint Oil, Mitcham.** With regard to this year's peppermint harvest, a producer known to us as reliable, informs us that by the 15th August the whole crop had been cut, and the distillation was in full swing, but that the latter did not last long, as the yield on the average was small. Only a few farmers express themselves as more satisfied. In consequence of the favourable weather-conditions the plants have developed extremely well, and yield an oil of excellent quality, but the area under cultivation is smaller than last year, and the total result of the distillation equally so. It diminishes from year to year, as much land is taken up for building purposes.

Reliable farmers declare that they only sell their oil to those persons who to their knowledge deal with it in the unadulterated state, and do not by means of adulteration make the quality to suit the price, so as to offer the oil abroad at a cheaper figure than they themselves have paid for it. Among the reliable English distillers who know the state of affairs, there exists great anxiety for the future of the peppermint industry, and we can only share this feeling, for at the present time the name "Mitcham" is in most cases only a cloak for oil-mixtures of all possible and impossible qualities.

The important purchases made by us through our London branch consist throughout of pure original qualities, which are characterised this year, owing to the favourable weather-conditions, by an exceptionally fine aroma.

**Peppermint Oil, Saxon, own distillate.** As in the English districts, the weather here was also very favourable for the cultivation of peppermint. The first harvest took place already at the end of July, the second at the end of August. The result of both was satisfactory in every respect, and we were able to produce this year not only a very considerable quantity, but also an oil of quite exceptional quality, which is equalled by no other kind.

Since we have recently succeeded in adding considerably to our landed property here, we will further increase our cultivation, and we hope to arrive gradually at a production and at a cost price which will enable us to compete seriously with the English oil. The mother-plants of our cultivation, as is well known, were obtained at the time at Mitcham.

Umney and Bennett<sup>1)</sup> report on the examination of Sicilian peppermint oil which had been distilled from cultivated plants at

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<sup>1)</sup> Chemist and Druggist 66 (1905), 945.

Messina, in order to determine whether the oil distilled from plants grown over there, shows noticeable differences from English and American peppermint oils, and whether the conditions of climate and soil had a special influence on the character of the oil.

It appears that the peppermint plants grow luxuriously at Messina and blossom early. In England the oil is usually distilled from plants which have not yet reached the flowering stage. Two distillates from fresh herb were prepared at Messina; the first in July, when the plants were still in full bloom; the second from herb which after the first crop had not yet come to full development, and did not yet show flower buds. The yield of oil from the second crop amounted to only one-third of that from the first. The low yield must partly be attributed to an early winter.

The difference in the properties of the two oils is very distinct. The oil obtained in July 1904 from the flowering herb (yield 0,4 %) gave the following results on examination:  $d$  0,908;  $n_D$  — 14°; total menthol 40%; free menthol 36,2%; ester 4,8% calculated as menthyl acetate. The oil was soluble in 4 volumes 70 per cent. alcohol, but did not congeal in a freezing mixture. The chemical composition of the oil has naturally a considerable influence on the physical constants.

The oil distilled in December 1904 from the second crop had the following properties:  $d$  0,920;  $n_D$  — 23°; total menthol 70,5%; free menthol 47,4%; ester (menthyl acetate) 29,4%; the oil was insoluble in 70 per cent. alcohol, in spite of rectification, but dissolved in two or more volumes 80 per cent. alcohol. The unusually high ester-content would appear to account for the insolubility in 70 per cent. alcohol. The small yield of this oil may perhaps be connected with its composition, but in any case it possesses a pleasant taste, and it greatly resembles in its properties the finest peppermint oil from white mint. Owing to the small yield this product would be comparatively expensive, but this year better results are anticipated, as the last season was particularly cold. The examinations published show clearly the great influence of climate and soil on the growth of the plants, and on the natural products formed by the latter. It would be of interest to continue the experiments, so as to see whether under altered conditions an oil can be obtained which corresponds to the finest English oil; such an oil would be very useful for the preparation of better-class confectionery, and of liqueurs.

**Petitgrain Oil.** It remains a matter of the greatest difficulty to induce the purveyors to make firm offers, as the situation in the Paraguay districts is too uncertain to enter into definite contracts. The transport of the oil from the interior to the ports of shipment alone often required several months. For example, a contract for delivery

in 1904 has only recently been completed. In agreement with the foregoing, the offers which a few years ago still exceeded the consumption, have now come to a complete stop, and the well-known Antwerp source which at the time endeavoured to monopolise this trade, has now completely come to an end. Recent reports from Paraguay announce that a hurricane has lately ravaged to such an extent the plantations supplying the petitgrain oil, that its prices have already commenced to rise.

According to a note in the German "Handelsarchiv", the value of the export in the year 1903 is said to have amounted to 35914 pesetas.

**Pine-needle Oils.** The commercial position of the oil from *Pinus montana*, which is nowadays used in large quantities, mixed with chloroform, as an embrocation, has during the last few months become even more critical, and we really do not know what will become of it in the coming winter when the distillation in the Alps is often interrupted for months. It is to be hoped that this cry of distress may lead to this, that the question is taken up in other districts. Many years ago there was a project of establishing distilling works in the Carpathian mountains, but this has unfortunately not been realised. The Siberian product is again available in sufficient quantity, since the situation in the producing districts has become sufficiently clear.

The following may be said with regard to the other conifer-distillates.

An oil from *Pinus montana* which attracted attention on account of its low price, was on closer examination found to be adulterated; it had namely been mixed with American turpentine oil, as may be concluded from the following examination-results:  $d_{15^{\circ}} 0,8682$ ;  $n_D + 6^{\circ} 43'$ ; ester number  $1,69 = 0,59\%$  bornyl acetate; soluble in 7 and more volumes 90 per cent. alcohol. There passed over on distillation (753 mm.): up to  $160^{\circ} = 34\%$ ; from  $160^{\circ}$  to  $165^{\circ} = 36$  per cent.; from  $165^{\circ}$  to  $170^{\circ} = 13\%$ ; from  $170^{\circ}$  to  $175^{\circ} = 3\%$ ; from  $175^{\circ}$  to  $190^{\circ} = 6\%$ ; residue  $= 8\%$ .

In the case of pure oil from *Pinus montana*, practically nothing passes over below  $160^{\circ}$  if the fractional distillation is carried on in the same manner.

A templin oil distilled by us at Bodenbach from the cones of *Abies alba* Miller, possessed a powerful limonene odour, and the following constants:  $d_{15^{\circ}} 0,8551$ ;  $n_D - 76^{\circ} 58'$ ; ester number  $2,44 = 0,85\%$  bornyl acetate; soluble in 7 and more volumes 90 per cent. alcohol.

**Rose Oil.** It is now confirmed that this year's result of the rose oil distillation in Bulgaria is smaller than that of last year. Reliable traders and distillers in the principal districts estimate it at:

	about	4150	kilos	
against	„	5000	„	in 1904
„	„	6200	„	„ 1903
„	„	3900	„	„ 1902
„	„	3200	„	„ 1901

Of the first-named quantity, fully half has probably already been sold, for up to 30<sup>th</sup> April (more recent statistics are not obtainable), 1025 kilos had already been shipped to the following countries: —

United States . . . . .	448	kilos
United Kingdom . . . . .	196	„
France . . . . .	127	„
Germany . . . . .	123	„
Russia . . . . .	44	„
Turkey . . . . .	39	„
Austria . . . . .	6	„
Switzerland . . . . .	5	„
Italy . . . . .	4	„
Belgium . . . . .	2	„
Holland . . . . .	1	„
Other countries . . . . .	30	„
<hr/>		
Total 1025 kilos.		

The tendency of the prices is upward, of course only for pure oil, which is the oil we quote for. The common commercial quality which is offered, even by middlemen, and unfortunately also in our neighbourhood, at 500 and 480 marks per kilo, is no criterion, for everyone who has some knowledge of this article knows that such prices are far below the market value of pure oil, and will prefer to prepare inferior qualities himself by admixture with artificial oil.

The trade in rose oil will be and remain a matter of confidence pure and simple until it is possible to establish practicable and absolutely certain data for judging the value of the oil, — a matter which is beset with exceptional difficulties in view of the peculiar chemical constitution of rose oil. The methods which we employ when purchasing rose oil demand already a considerable amount of chemical knowledge, much skill, and still more experience. For this reason they can be utilised by experts only.

According to the most recent reports from Kazanlik and Karlovo, pure rose oil is now maintained at 600 marks per kilo, and at that price bought on speculation. It is believed that the stocks of this oil will soon be exhausted, and it is recommended to cover the requirements at an early date. We have already several months ago



December harvest on the island of Iesing (Dalmatia)



laid in an abundant stock, and, taking the wretched circumstances into consideration, supply the oil in the original condition at the smallest possible profit.

**Rose Oil, own distillate.** This year's rose harvest has taken place under particularly favourable conditions. Rain and sunshine alternated in a manner that left nothing to be desired, and helped to mature a blossom material as abundant as it was excellent. After executing the orders on hand, we have about 12 kilos rose oil left, and about 1000 kilos rose pomade. Rose water is now also again available in sufficient quantities. For export we recommend, with a view to saving carriage and duty, the concentrated kind which is prepared in the exact proportion of 6 kilos roses to 1 kilo water.

A retrospective work on the more important examinations of the constituents of rose oil has been published by M. v. Waldheim<sup>1)</sup>. As the work of the individual authors has already been partly taken into account in the preparation of Gildemeister and Hoffmann's work "The Volatile Oils", and partly been mentioned in our Reports, it will suffice to refer to the publication of the above treatise, which contains numerous bibliographical notes.

**Rosemary Oil.** The French distillate is now somewhat cheaper; the result of the distillation is said to have been a normal one.

The Dalmatian distillers attempted to carry through a rise in the prices, but owing to the low value of the French oil they soon became more accommodating, and made contracts at last year's prices. The export of Dalmatian oil to France may possibly experience a considerable drop this year. We have succeeded, not without a good deal of trouble, in obtaining a few photographic views from the distillation districts on the island of Lesina, two of which we here place before our readers.

An oil imported from Tunis differs somewhat in its properties from ordinary rosemary oil, and might therefore possibly not be considered a competing product of equal value to the French oil; the differences are probably due to the fact that for the production of the oil not only *Rosmarinus officinalis* L., but also other plants have been used. The clear, almost colourless distillate possesses an odour resembling rosemary, and reminding of spike oil:  $d_{15^\circ}$  0,9171;  $n_D + 2^\circ 17'$ ;  $n_D$  of the first 10% of the distillate —  $2^\circ 24'$ ; soluble in 1 and more vol. 30 per cent. alcohol.

<sup>1)</sup> Zeitschr. Allgem. Österr. Apoth. Ver. **43** (1905), 633 and 657.

**Oil of Muscatel Sage.** The fresh blossoms and stems of the plants *Salvia sclarea* L. grown in Miltitz, yielded on distillation 0,117% of a bright olive-green oil with a peculiar odour. The other properties of this oil are as follows:  $d_{15}^{\circ}$  0,9209;  $\alpha_D$  —  $23^{\circ}38'$ ;  $n_{D20}^{\circ}$  1,47724; acid number 0,9; ester number 153,0; ester number after acetylation 154,9; soluble in 1,5 vol. 80 per cent. alcohol with slight opalescence, when more solvent is added with separation of paraffin; makes with 90 per cent. alcohol at first a clear mixture, when about 3 volumes and more are added cloudiness occurs, with separation of paraffin.

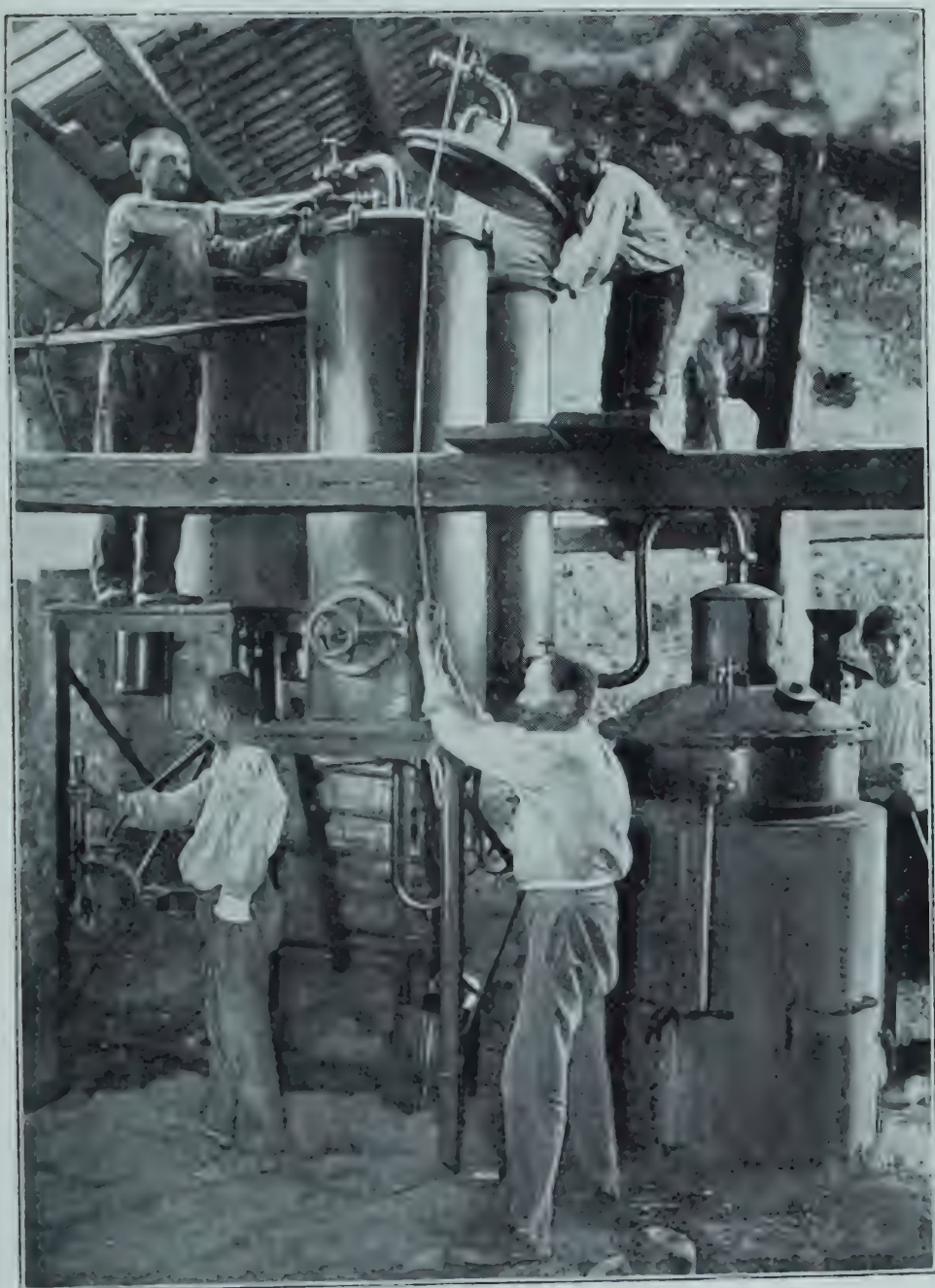
For the purpose of producing l- $\alpha$ -thujone, Wallach<sup>1)</sup> examined a laevorotatory sage oil obtained from large-leaved sage. But contrary to ordinary sage oil (from *Salvia officinalis*) which in addition to d- $\alpha$ - contains chiefly d- $\beta$ -thujone, it contained no trace of thujone. On the other hand much l-camphor could be detected besides pinene and cineol. From one fraction, a crystallised body of the melting point  $85^{\circ}$  to  $86^{\circ}$  could be separated by means of nitrous acid, which did not behave like one of the known phellandrene nitrites.

We have received a small sample of sage oil which had been distilled from plants grown on Mount Carmel (Palestine). Unfortunately we miss definite information on the botanical origin of the oil, which resembles in its properties the oil free from thujone examined by Wallach mentioned above. As the quantity of the water-white oil with a camphor-like odour was insufficient for a thorough examination, we must confine ourselves to the enumeration of the following data:  $d_{15}^{\circ}$  0,9175;  $\alpha_D$  —  $9^{\circ}35'$ ;  $n_{D20}^{\circ}$  1,46734; ester number 7,3; forms no clear solution in 10 volumes 70 per cent. alcohol; soluble in 1 and more volumes 80 per cent. alcohol.

**Sandalwood Oil, East Indian.** The value of this important article has on the whole remained unchanged, and the condition of permanence which now prevails proves that, generally speaking, the limits of productive power have been reached. In spite of our higher quotations, corresponding to the increased prices of the wood, we were scarcely able to produce enough oil to meet the current demand.

We are informed that the annual auction sales of sandalwood of the Mysore State will be held at the undermentioned places on the dates specified against each: —

<sup>1)</sup> Nachr. K. Ges. Wiss. Göttingen 1905, part 1, 1.



Distillation of rosemary oil on the island of Lesina (Dalmatia).



District	Koti	Date of Auction Sale	Approximate quantity in tons	Remarks
Shimoga	Tirthahalli	14 <sup>th</sup> Nov. 1905	200	Includes Kadur District wood
do.	Sagar	18 <sup>th</sup> Nov. 1905	200	
do.	Shimoga	22 <sup>nd</sup> Nov. 1905	370	Includes Chitadrug and Kadur District wood
Kadur	Tarikere	25 <sup>th</sup> Nov. 1905	150	
do.	Chikmagalur	28 <sup>th</sup> Nov. 1905	350	Includes Kodar and Tumkur District wood
Hassan	Hassan	2 <sup>nd</sup> Dec. 1905	200	
Bangalore	Bangalore	6 <sup>th</sup> Dec. 1905	130	
Mysore	Seringapatam	9 <sup>th</sup> Dec. 1905	250	
do.	Hunsur	12 <sup>th</sup> Dec. 1905	450	
Total 2300				

The shipments of sandalwood during the season 1904 to 1905 amounted to the following: —

	from Tellicherry	14998 cwts.
	„ Calicut	7872 „
	„ Mangalore	8874 „
	Total	31744 cwts.,
against		

30448	cwts. in	1903—1904
24166	„ „	1902—1903
22437	„ „	1901—1902
22114	„ „	1900—1901.

The continual increase in the exports shown by the above figures confirms the growing consumption in a striking manner. To express this increase in the quantity of oil, the figures of the present year's export would be equivalent to about 64000 kilos sandalwood oil, of a value of 1400000 marks in round figures. It is here assumed that the above export figures do not include the quantities of wood shipped to Chinese ports.

How important and growing the consumption of sandalwood is in China itself, appears also from the fact that the quantities imported in the comparatively small commercial port of Shasi were,

in 1900	429	piculs
„ 1901	492	„
„ 1902	1498	„
„ 1903	1600	„

Of the Australian Swan-river sandalwood, Eastern Asia also consumes considerable quantities. The shipments in the year 1903 were:

to China	£ 21399
„ Singapore	„ 6727
„ Hong Kong	„ 9787
Total	£ 37913,

whilst in 1902 the total value came to as much as £ 61771.

The importance of the "spike" disease of the sandal trees in Mysore, to which we have repeatedly referred in our previous Reports, appears, according to information received recently, to have been overestimated; we at least are informed that the production of sandalwood would probably not diminish for a considerable number of years. The Forest Department, so it is said, now proceeds in this manner in collecting the wood, that it no longer (as in previous years) removes first of all the trees which have died from the disease, and only makes up the shortage with healthy full-grown trunks, but on the contrary at present fills up the required quantity by trees which must be cut down because they have been attacked by the disease. As a matter of fact, less than half the number of diseased trees can be used at all, as they are mostly not strong enough in timber, but in any case the removal of numerous diseased trees is bound to prevent effectually the propagation of the spike-disease. It is further reported that formerly much damage was done to the young sandal plantations by herds of goats, whilst now steps have been taken to keep all herds away from the plantations, and a successful development is thus ensured to the young trees.

We have previously, on the strength of the behaviour of our own distillates, specified that East Indian sandalwood oil must have a rotatory power of at least  $-17^{\circ}$ . In future we shall not be able to adhere to this strictly; on the contrary, slight deviations are permissible. We have, namely, recently obtained from 22500 kilos sandalwood a distillate which had a slightly lower rotation and possessed the following properties:  $d_{15^{\circ}} 0,9794$ ;  $\alpha_D -16^{\circ}30'$ ; acid number 3,5; ester number  $17,4 = 6,8\%$  ester santalol; ester number after acetylation  $199,4 = 92,1\%$   $C_{15}H_{24}O$ ; soluble in about 4,5 volumes 70 per cent. alcohol with slight opalescence, which soon disappears when more solvent is added.

Charles E. Vanderkleed<sup>1)</sup> calls attention to two slight errors which occur in the statement of the santalol-determination in Gilde-

<sup>1)</sup> American Druggist 47 (1905), 8.

meister and Hoffmann's work "The Volatile Oils". In the one case it is simply a question of a misprint<sup>1)</sup>, as in the place of the factor 0,42 in the formula given for the calculation, 0,042 should have been given. The second error denounced by Vanderkleed consists of this, that for the saponification only normal potash liquor is prescribed. What is meant here is of course alcoholic normal potash liquor, which for the rest is already evident from the chapter on the examination of essential oils. We also use a solution for common salt for washing all acetylated oils, instead of water. A further error occurs where the same method is mentioned in the English edition<sup>2)</sup> of our Report; this error has crept in the translation, for in our German edition<sup>3)</sup> acetic acid anhydride is quite correctly indicated for the acetylation, whilst in the process of translating this has become acetic acid.

**Oil of Schinus.** The phellandrene contained in oil of schinus (*Schinus molle* L.), was recently recognised by Wallach<sup>4)</sup> as consisting chiefly of d- $\alpha$ -phellandrene. It is an open question whether it also contains small quantities of  $\beta$ -phellandrene.

**Spike Oil.** This oil which last year fetched prices far above its real value, was at first, towards the end of August, quoted low; but before it was possible to enter into contracts, it was bought up by French firms at exaggerated prices, and we are informed that it will soon again be driven up to the high level of last year.

We have kept ourselves completely free from this movement, as an abundant stock enabled us to watch calmly the course of events. The result of the harvest does not justify such a bullish movement.

**Star-anise Oil.** The prices of this important article have changed little during the last six months, but they appear to be at present on the way to an improvement. According to information from the producing districts, incessant rain in the month of May has done great damage to the trees, and it is believed that the result will not be ahead of that of last year.

The movement of the prices is influenced to a considerable extent by the stocks in hand in Europe, which, however, cannot be controlled.

<sup>1)</sup> Comp. Report April 1897, 40.

<sup>2)</sup> Report 1897, 36.

<sup>3)</sup> Bericht April 1897, 40.

<sup>4)</sup> Nachr. K. Ges. Wiss. Göttingen 1905, part. I, 2.

The imports by sea into Hamburg were:

	1904			1903	
	Kilos	Marks		Kilos	Marks
from China . . . . .	30140	282020	against	9150	88120
„ Japan . . . . .	3600	29900	„	—	—
„ the United States on the Atlantic side . . . . .	—	—	„	210	2560
„ France . . . . .	16990	145810	„	15070	115950
„ the United King- dom . . . . .	1310	12980	„	5570	51040
total, by sea,	52040	470710	against	30000	257670

The first-named quantity equals about 1730 cases, against 1000 cases in 1903. Our share of the 1904 imports was 940 cases.

The United States of America imported in 1904: 110049 lbs. or about 1658 cases of a value of 72497 dollars. The shipments in 1905 show a decided falling off. They amounted, for star-anise and cassia oils together, from 1<sup>st</sup> January to end of May:

to the United Kingdom 251 cases against 424 cases in 1904

„ „ Continent 688 „ „ 1137 „ „ 1904,

of which quantities probably about three-fifths belong to star-anise.

**Oil of *Tanacetum boreale*.** The oil of *Tanacetum boreale* Fisch. which we had already distilled before<sup>1)</sup>, has now been obtained by us from the fresh herb; the distillate obtained, (yield 0,117%) behaves in a slightly different manner to the oil produced at the time from the half-dried herb. It is somewhat more viscid, has a green-brown colour, and a strong thujone odour;  $d_{15}^{\circ}$  0,9603; rotatory power could not be determined owing to the dark colour of the oil;  $n_{D20}^{\circ}$  1,49167; acid number 30,47; ester number 40,55; not soluble in 10 volumes 70 per cent. alcohol; soluble in 2 volumes 80 per cent. alcohol, when more solvent is added cloudiness occurs, with separation of paraffin; can be mixed with 90 per cent. alcohol, until when 0,8 vol. are added, cloudiness occurs owing to separation of paraffin.

**Thuja Oil.** During the production of the semicarbazone from l-fenchone of thuja oil, Wallach<sup>2)</sup> found that this fenchone contained camphor. As the camphor cannot be removed by means of the usual purification-process of the fenchone (treatment with nitric

<sup>1)</sup> Report October 1904, 97.

<sup>2)</sup> Nachr. K. Ges. Wiss. Göttingen 1905, No. I, 11.

acid), Wallach made use of the property of camphor of very readily forming a semicarbazone, for the purification of the fenchone. This discovery led to an examination of thuja oil, which showed that the oil contains l-borneol, or esters of l-borneol, which are converted into l-camphor when the fenchone is worked out in the usual manner with the use of oxidation agents.

**Thyme Oil.** With this article we have also had occasion to observe some adulterations. In one case it was a question of an oil which had been doctored with oil of turpentine; it was particularly striking on account of its deficient solubility, and low phenol-content. The result of the examination was as follows:  $d_{15^\circ} 0,8919$ ;  $\alpha_D - 2^\circ$ ; phenol-content 12,5 %; not soluble in 10 volumes 80 per cent. alcohol, separation of oil on the surface.

Another sample designated as "white" thyme oil had probably been mixed with a considerable quantity of camphor oil, as may be concluded from its properties:  $d_{15^\circ} 0,8927$ ;  $\alpha_D + 12^\circ$ ; phenol-content about 12 %; soluble in 7 to 8 volumes and more 80 % alcohol. As the "white" thyme oils of commerce are very often adulterated, the consumers should now at last discontinue specifying thyme oil to be absolutely colourless.

**Turpentine Oil.** A Greek oil of turpentine which we had an opportunity of examining showed similar properties to the oils<sup>1)</sup> examined by Utz and Dambergis. Our results were as follows:  $d_{15^\circ} 0,8631$ ;  $\alpha_D + 38^\circ 41'$ ;  $n_{D20^\circ} 1,46555$ ; ester number 4,5; soluble in 5,5 to 6 volumes 90 per cent. alcohol. On fractional distillation (at 754 mm.) there passed over: from  $152^\circ$  to  $156^\circ = 6\%$ ; from  $156^\circ$  to  $157^\circ = 28\%$ ; from  $157^\circ$  to  $158^\circ = 10\%$ ; from  $158^\circ$  to  $159^\circ = 30\%$ ; from  $159^\circ$  to  $160^\circ = 16\%$ . Residue 10 %.

In connection with our remarks<sup>2)</sup> on the definition "turpentine oil", under which name we wish to understand exclusively steam-distillates from turpentine, Utz<sup>3)</sup> recommends the following wording for the next Edition of the German Pharmacopœia: "The essential oil obtained by distillation with steam from the turpentine of various American and French species of *Pinus*". This would at the same time denote the only commercial qualities which come under consideration for pharmaceutical and medicinal purposes. We have already stated that, according to our above definition of turpentine oil, we naturally cannot recognise as oil of turpentine the oil which is obtained with super-

<sup>1)</sup> Report April 1905, 79.

<sup>2)</sup> Report April 1905, 89.

<sup>3)</sup> Pharm. Centralh. 46 (1905), 681.

heated steam<sup>1)</sup> from wood rich in turpentine. We therefore agree on this point with Utz. Although in technical circles frequently no definite distinction is made in the designation of turpentine oils and pine tar oils, such differentiation is yet necessary, as especially those properties of the two oils which are important for technical purposes, such as solubility, oxidation behaviour on the air, etc. differ very considerably.

In our last Report<sup>2)</sup> we communicated a note on the production of turpentine in India, and to-day we are able to give in connection therewith information on the properties of Indian turpentine and of the oil obtained from it. Whilst the Burmese turpentine oils previously examined by Armstrong<sup>3)</sup> (from *Pinus Khasya* and *Pinus Merkusii*) which were said to be of equal value as the American and French oils of turpentine, have not become particularly important for commerce, the turpentine which has recently been obtained from *Pinus longifolia* Roxb., and which yields from 72 to 77 % resin and 14 to 18 % turpentine oil, appears to have a better future. The following data are abstracted from a work on the last-named products by Frank Rabak<sup>4)</sup>. Indian turpentine is white, opaque, and of a very sticky granular composition, which is probably due to crystals of resin acid which have separated out. The turpentine-like odour is peculiarly pleasant, and reminds somewhat of limonene. On distillation with water-vapour Rabak obtained 18,5 % essential oil which possessed a characteristic pinene odour, whilst the odour of limonene could also be perceived. The turpentine examined had the following properties:  $d$  0,960;  $[\alpha]_D - 7^\circ 42'$ ; acid number 129; ester number 11; saponification number 140. The constants of the oil obtained from it were  $d$  0,866;  $[\alpha]_D + 2^\circ 48'$ . The examination of the resin gave  $\alpha_D - 1^\circ 10'$  (100 mm tube, 10 per cent. solution); acid number 142; ester number 13; saponification number 155. On fractional distillation of the oil, Rabak obtained the following results:

1. fraction	165° to 170°	56 %	$\alpha_D - 2^\circ$
2.     "	170°   " 175°	20 %	$\alpha_D + 2^\circ 48'$
3.     "	175°   " 180°	9 %	$\alpha_D + 6^\circ 50'$
4.     "	180° and higher	15 %	$\alpha_D + 18^\circ 12'$

In our last Report<sup>5)</sup> we discussed a process employed in Finland for the production of turpentine oil which differs from the methods

<sup>1)</sup> This Report, p. 69.

<sup>2)</sup> Report April 1905, 78.

<sup>3)</sup> Gildemeister and Hoffmann, "The Volatile Oils", p. 263.

<sup>4)</sup> Pharmaceut. Review **23** (1905), 229.

<sup>5)</sup> Report April 1905, 79.

hitherto used, and we then came to the conclusion that it was inadmissible to designate such a product with the name of turpentine oil, as it is nothing but pine tar oil. A further, newer process, introduced by the engineer Elfstroem, and possibly valuable for forest-culture, is said to make it possible to produce a turpentine oil which is in no way inferior to the best French oil of turpentine, as in this process a temperature which imparts a bad odour to the oil is obviated. According to a report by Utz<sup>1)</sup> the distillation is carried out as follows: Water vapour issuing from a small boiler, is brought to a definite temperature of several hundred degrees in a superheating apparatus, and conducted into a horizontal retort of 5 cubic metres capacity which is filled with a pine wood rich in resin, and is closed. The distillation of the wood soon commences, and the wood-tar mixed with condensation-water, is collected at the bottom of the retort, whilst the volatile products with water vapours enter a tube fitted to the top of the retort, pass through a second superheater, and then enter a second retort where the process commences afresh and proceeds in exactly the same manner as in the first retort. In precisely the same way the vapour may pass through still more retorts before it is allowed to enter the condensing worm. The wood tar collecting at the bottom of the retorts is from time to time drawn off. The wood gases passing over with the water vapour and the volatile products are conducted into the heating chamber of the boiler, and used for heating. The turpentine oil is finally separated from the distillation water simply by allowing it to settle in an apparatus consisting of numerous chambers. For the purpose of separating the tar from the distillation water, salt is added to the aqueous emulsion.

We are of opinion that even this oil obtained by the new process is not entitled to the name turpentine oil; this name should be exclusively reserved for the steam-distillates from turpentine. It is a question for the purchaser, to insist that only such distillates shall be supplied to him as oil of turpentine.

Utz<sup>2)</sup> has occupied himself in a more detailed manner with the examination of turpentine oil. An oil of turpentine obtained by dry distillation of wood had the following properties:  $d_{15}^{\circ}$  0,861; polarisation in a 200 mm. tube  $+33^{\circ} 92'$ ;  $n_{D15}^{\circ}$  1,4723. The bulk of the oil passed over on fractional distillation from  $160^{\circ}$  to  $162^{\circ}$ , and up to  $165^{\circ}$ ; the refraction of the distillates up to  $165^{\circ}$  amounted at  $15^{\circ}$  to 1,472, that of the residue to 1,4798.

<sup>1)</sup> Pharm. Centralh. **46** (1905), 299, according to Chem. Revue über Fett- und Harzindustrie **1904**, 154.

<sup>2)</sup> Chem. Rev. Fett- und Harz-Ind. **12**, 71 to 73 and 99 to 100. According to Chem. Centralbl. **1905**, I. 1673.

The characteristics for identification of turpentine oils obtained by different processes, which Sundwik<sup>1)</sup> has described (odour and reaction-capacity towards chlorine and iodine), are not considered by Utz as absolutely reliable. He likewise rejects as too troublesome the method recommended by Mc. Candles<sup>2)</sup> for the detection of petroleum products in oil of turpentine, which is based on the polymerisation with concentrated or fuming sulphuric acid and subsequent steam-distillation; on the other hand, he recommends the determination of the refraction of the portion of turpentine oil which is insoluble in fuming sulphuric acid, which may possibly supply useful indications for judging oil of turpentine.

For the purpose of distinguishing turpentine oil from pine tar oil, the reaction observed by Herzfeld<sup>3)</sup> (shaking of equal volumes of oil and a solution of sulphurous acid, when the layer of oil, in the presence of pine tar oil, acquires a yellowish green colour) is generally useful. Utz also employs for this purpose the following reaction: Equal volumes of the oil in question and official solution of stannous chloride are mixed. Whilst in the case of Austrian turpentine oil the reagent became yellow, the oil colourless; with Greek, the reagent orange, the oil yellow, and with American turpentine oil the reagent orange and the oil yellow, the solution of stannous chloride acquired with all kinds of pine tar oil a raspberry red colour; the oil remained mostly yellow, but in many cases the oil itself also coloured raspberry red. With a few kinds of oil there occurred then the brown or black coloration (Lyons reaction with concentrated hydrochloric acid). The reaction also took place in mixtures of pine tar oil with turpentine oil, and also with substitutes. The latter, petroleum distillates or benzene preparations, did not react. The future will show how these colour-reactions, which we consider on the whole with a sceptical eye, will answer.

E. Valenta<sup>4)</sup> has examined with regard to their optical properties fractions of pinolin (resin essence) which are suitable for the adulteration of turpentine oil, and he comes to the conclusion that the refractive and rotatory powers of the fractions in question can hardly be used for detecting an addition of pinolin to oil of turpentine. But the fractions of pinolin show Herzfeld's sulphurous acid reaction (yellow coloration when shaken with a solution of sulphurous acid) which pine tar oil, as is well known, also gives. In order to provide the most certain proof of the addition of pinolin to turpentine oil, the oil is fractionated and the portions passing over below 160° are

<sup>1)</sup> Report April 1905, 79.

<sup>2)</sup> Report April 1905, 80.

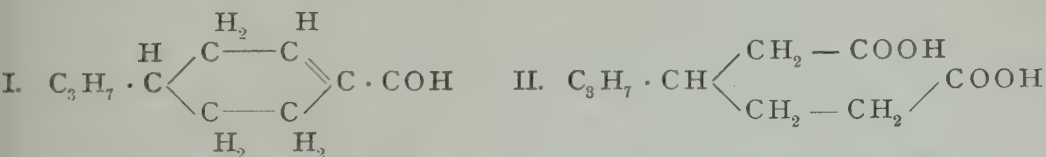
<sup>3)</sup> Report April 1905, 78.

<sup>4)</sup> Chemiker-Zeit. 29 (1905) 807.

used according to Valenta for the following reactions: The portions of pinolin distilling over up to  $160^{\circ}$  give an intensive green colour when acetic anhydride and one drop sulphuric acid are added; these fractions further show intense green to olive-green colorations, if 1 part is mixed with 1 to 2 parts of a 6 per cent. solution of iodine in chloroform or carbon tetrachloride and carefully heated over the flame of a Bunsen burner or in a water-bath.

According to Valenta's researches the "pine tar oils" have all a higher refractive power than pure oils of turpentine. This also applies to refined pine-tar oils, inasmuch as  $n_{D20,5^{\circ}}$  is usually found above 1.471, a figure which pure turpentine oils seldom reach. As a distinguishing reaction between pine-tar oil and turpentine oil, Valenta mentions the following: if equal volumes of 1 per cent. gold chloride solution and oil of turpentine are shaken in a test tube, placed on the waterbath, heated for one minute, and the test tube is then removed and shaken, pure turpentine oils only show a separation of gold in the oil film. The solution itself does not become discoloured. The oils of the pine tar oil group, whether refined or not, and also pinolin, discolour the gold solution completely; this discoloration occurs most rapidly in the case of pinolin.

**Waterfennel Oil.** On the strength of our examination we had already expressed the surmise that the aldehyde  $C_{10}H_{16}O$  "phellandral" detected by us in this oil, is a tetrahydrocuminic aldehyde. By an oversight it was printed in our Report of October 1904, p. 90 "in which the double-linking is situated in the  $\beta$ ,  $\gamma$ -position towards the aldehyde group" instead of (correctly) " $\alpha$ ,  $\beta$ -position"; for only an aldehyde of formula I can yield on oxidation a dibasic acid  $C_9H_{16}O_4$  (formula II), if not (as Wallach<sup>1</sup>) supposes) during the oxidation a displacement of the double linking to the aldehyde- or carboxyl-group takes place, a supposition for which we had no grounds previous to the publication of Wallach's experiments on  $\beta$ -phellandrene.



**Wintergreen Oil.** For the purpose of comparing the properties of authentic pure wintergreen oils with the requirements of the new American Pharmacopœia, E. F. Ziegelmann<sup>1</sup>) has submitted to distillation both the bark of *Betula lenta* L., and the leaves of *Gaultheria procumbens* L. As neither of these oils occur as such in the plants, but are present in the form of non-odorous glucosides,

<sup>1</sup>) Compare the present Report, p. 98.

which must be split up by a ferment before the commencement of the distillation, it was a matter of particular interest to decide what the most favourable conditions are for the production of the oils. When experimenting with small quantities Ziegelmann obtained the best yields after twelve hours maceration at ordinary temperature, namely of birch bark oil 0,62%, of wintergreen oil 1,57%. Prolonged maceration did not affect the yield; by maceration at 40° to 50° it became somewhat less; on distillation without maceration the yield was considerably lower. When larger quantities were worked up, birch bark gave a yield of 0,306%; by means of cohobation a further 0,076% were obtained from the distillation waters. Both oils formed clear solutions with 4 volumes 70 per cent. and also with 1 volume 80 per cent. alcohol. Wintergreen leaves, when distilled on a large scale, only yielded 0,633% oil of which 0,2889% were obtained direct, and 0,344%<sup>2)</sup> by cohobation. Both oils were miscible in every proportion with 90 per cent. alcohol; of 80 per cent. alcohol 2 volumes sufficed, and of 70 per cent. 7 volumes. The specific gravity and the ester-content fluctuated, according to the method of production and purification, in the case of birch bark oil between 1,1502 and 1,171 (at 25°), and 90,2 to 97,83% ester, and in gaultheria oil between 1,175 and 1,185, and 96,20 and 97,13% respectively.

**Ylang-Ylang Oil.** The condition of the market during the last few months was more animated than at the beginning of the year. The accumulated stocks were mostly sold, and at the present time there is practically no stock of the brand *Sartorius*, and only unimportant consignments are on the way. We do all we can to meet the requirements of our regular clients, but would beg that the continued scarcity of this brand be taken into consideration, and orders be sent in good time.

A recent mail from Manila has brought the news that the typhoon of September 26<sup>th</sup> last has seriously damaged the Ylang Ylang trees; the arrivals of flowers have at once diminished, higher prices being asked, and raised quotations for the oil are likely to follow.

Second qualities of natural oil are offered in abundance, and are difficult to sell; these are unable to compete with the artificial ylang-ylang oil which is far finer, and has a much more flowery perfume, and they are often replaced by cananga oil, or mixtures of the latter and artificial ylang-ylang oil. According to the *Monthly Summary of Commerce of the Philippine Islands*, the exports from Manila were:

in the year	1902/1903	of a value of	\$ 103 789
" "	" 1903/1904	" " " "	" " 103 247

<sup>1)</sup> Pharmaceut. Review 23 (1905), 83.

<sup>2)</sup> The figures 0,383 appearing in the original are probably due to a misprint or miscalculation.

that is to say, in round figures  $\frac{1}{2}$  million marks of ylang-ylang oil of all qualities.

**Ylang-Ylang Oil "Schimmel & Co."** (German Patent No. 142859). The use of this product which was introduced by us into commerce in 1896<sup>1)</sup> as the first artificial ylang-ylang oil, is constantly growing, and it enables the perfumer to employ this valuable aromatic substance, which formerly could only be used for the highest-class scents, now also for products sold at medium prices.

The use of ylang-ylang oil has become exceptionally extensive, particularly through the introduction of the artificial oil, and there are few compositions in which it does not play a more or less important part.

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## Novelties.

**Oil of *Eryngium campestre* L. (*Umbelliferae*).** The oil obtained by a business friend in the South of France from the fresh herb in a yield of 0,088%, has a faint yellow colour, and a pleasant undetermined odour distantly reminding of oil of ambrette seeds;  $d_{15}^{\circ}$  0,9043;  $\alpha_D$  —  $5^{\circ}42'$ ;  $n_{D20}^{\circ}$  1,48518; ester number 10,47; insoluble in 10 volumes 80 per cent. alcohol; soluble in 1 volume and more 90 per cent. alcohol; the dilute solution has a feeble opalescence. We do not believe that this oil is suitable for practical purposes.

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## The new American Pharmacopœia.

We have now for some years made it a habit to submit to a detailed discussion in our Reports those articles in the new editions of the Pharmacopœias which come under consideration for our purposes. At the present moment, when the eighth edition of the American Pharmacopœia which has come into force on the 1<sup>st</sup> September 1905, has made its appearance, we will not depart from this rule, and will supplement or correct, as the case may be, various details in accordance with our experience. Unfortunately the new Pharmacopœia has reached us so late, that a detailed discussion in our present Report was not possible. For this reason we confine ourselves at the moment to the enumeration of the requirements specified by the Pharmacopœia, and will return to the details in our next Report.

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<sup>1)</sup> Report April 1896, 66.

With regard to the general information, it may be pointed out that the specific gravities are given for a temperature of  $25^{\circ}\text{C}$ ., compared with water at the same temperature. In this Pharmacopœia the temperature of  $25^{\circ}\text{C}$ . has, as a matter of fact, been taken as standard temperature wherever solubility, specific gravity, and volumetric operations are mentioned; only for alcohol and wine,  $60^{\circ}\text{F}$ . ( $15,667^{\circ}\text{C}$ .) has been taken as the standard temperature, for reasons of expediency.

Of alcohols, the American Pharmacopœia mentions, besides the absolute alcohol which must not contain more than 1 per cent. by weight of water, also the ordinary alcohol (with 92,3 per cent. by weight or 94,9 per cent. by volume) and the dilute alcohol (with 41,5 per cent. by weight or 48,9 per cent. by volume pure alcohol).

**Benzaldehydum** (*Benzaldehyde*). Colourless, strongly refractive liquid, with at least 85 % pure benzaldehyde;  $d_{25^{\circ}}$  about 1,045; boiling point  $179^{\circ}$  to  $180^{\circ}$ ; optically inactive; soluble in alcohol in every proportion.

**Camphora** (*Camphor*). White transparent mass;  $d_{25^{\circ}}$  0,990; dextro-rotatory; melting point  $175^{\circ}$ ; boiling point  $204^{\circ}$ .

**Cinnaldehydum** (*Cinnamic Aldehyde*). Colourless liquid with at least 95 % pure cinnamic aldehyde;  $d_{25^{\circ}}$  about 1,047; optically inactive; boils about  $250^{\circ}$  with decomposition; solidifies in a freezing mixture, and melts again at  $-7,5^{\circ}$ ; soluble in alcohol in every proportion.

**Eucalyptol**. Colourless liquid;  $d_{25^{\circ}}$  0,925; boiling point  $176^{\circ}$  to  $177^{\circ}$ ; optically inactive; congeals on cooling into needle-shaped crystals, which melt at  $-1^{\circ}$ ; soluble in alcohol in every proportion.

**Eugenol**. Colourless or faintly yellow liquid;  $d_{25^{\circ}}$  1,072 to 1,074; miscible with alcohol in every proportion; soluble in 2 parts 70 per cent. alcohol; boiling point  $251^{\circ}$  to  $253^{\circ}$ ; optically inactive.

**Menthol**. Colourless, needle-shaped or prismatic crystals; melting point  $43^{\circ}$ ; boiling point  $212^{\circ}$ ; alcoholic solution neutral, and lævo-rotatory.

**Methylis salicylas** (*Methyl Salicylate*). Colourless liquid;  $d_{25^{\circ}}$  1,180 to 1,185; boiling point  $219^{\circ}$  to  $221^{\circ}$ ; optically inactive; soluble in alcohol in every proportion.

**Oleum amygdalae amarae** (*Oil of Bitter Almond*). Colourless or yellow, strongly refractive liquid. Content of benzaldehyde at least 85 %; content of hydrocyanic acid not below 2 % and not above 4 %;  $d_{25^{\circ}}$  1,045 to 1,060; boiling point  $180^{\circ}$ ; optically inactive; soluble in alcohol in every proportion, also in equal volume 70 per cent. alcohol.

**Oleum anisi** (*Oil of Anise*). Colourless or faintly yellow liquid;  $d_{25^{\circ}}$  0,975 to 0,985; lævorotatory, at  $25^{\circ}$  in a 100 mm. tube  $-2^{\circ}$ ; soluble in equal volume alcohol, and in 5 volumes 90 per cent. alcohol; congealing point not below  $15^{\circ}$ .

**Oleum aurantii corticis** (*Oil of Orange Peel*). Faintly yellow oil;  $d_{25^{\circ}}$  0,842 to 0,846; optical rotation not below  $+95^{\circ}$  in a 100 mm. tube at  $25^{\circ}$  C.

**Oleum betulae** (*Oil of Betula*). Optically inactive.

**Oleum cadinum** (*Oil of Cade*). Brownish or dark-brown liquid; almost insoluble in water, but imparting to it an acid reaction; only partly soluble in alcohol; completely soluble in ether.

**Oleum cajuputi** (*Oil of Cajuput*). Colourless or greenish liquid with at least 55% cineol:  $d_{25^{\circ}}$  0,915 to 0,925; miscible in every proportion with alcohol; soluble in 1 part 80 per cent. alcohol; lævorotatory, not more than  $-2^{\circ}$  in a 100 mm. tube at  $25^{\circ}$  C.

**Oleum cari** (*Oil of Caraway*). Colourless or pale yellow;  $d_{25^{\circ}}$  0,905 to 0,915; soluble in the same volume alcohol, and in 3 to 10 volumes 80 per cent. alcohol;  $\alpha_{D25^{\circ}}$   $+70^{\circ}$  to  $+80^{\circ}$  in a 100 mm. tube.

**Oleum caryophylli** (*Oil of Cloves*). Colourless or pale yellow liquid with at least 80 per cent. by volume eugenol;  $d_{25^{\circ}}$  1,040 to 1,060; soluble in an equal volume alcohol, and in about 2 volumes 70 per cent. alcohol.

**Oleum chenopodii** (*Oil of Chenopodium*). Colourless or yellow;  $d_{25^{\circ}}$  about 0,965 to 0,985; soluble in 5 volumes 70 per cent. alcohol; lævorotatory,  $\alpha_{D25^{\circ}}$  not above  $-5^{\circ}$  in a 100 mm. tube.

**Oleum cinnamomi** (*Oil of Cinnamon, Oil of Cassia*). Yellowish or brownish liquid, containing at least 75 per cent. by volume cinnamic aldehyde;  $d_{25^{\circ}}$  1,045 to 1,055; almost inactive, not more than one degree to the right or left; when observed in a 100 mm. tube; soluble in 2 volumes 70 per cent. alcohol.

**Oleum copaibae** (*Oil of Copaiba*). Colourless or pale yellow;  $d_{25^{\circ}}$  0,895 to 0,905; lævorotatory; soluble in 2 volumes alcohol.

**Oleum coriandri** (*Oil of Coriander*). Colourless or faintly yellow;  $d_{25^{\circ}}$  0,863 to 0,878; soluble in 3 volumes 70 per cent. alcohol; soluble in every proportion in 80 and 90 per cent. alcohol;  $\alpha_{D25^{\circ}}$  from  $+7^{\circ}$  to  $+14^{\circ}$ .

**Oleum cubebae** (*Oil of Cubebs*). Colourless, pale green, or yellow;  $d_{25^{\circ}}$  0,905 to 0,925,  $\alpha_{D25^{\circ}}$   $25^{\circ}$  from  $-25^{\circ}$  to  $-40^{\circ}$ .

**Oleum erigerontis** (*Oil of Erigeron*). Faintly yellow;  $d_{25^{\circ}}$  0,845 to 0,865; soluble in an equal volume alcohol,  $\alpha_{D25^{\circ}}$  about  $+50^{\circ}$ .

**Oleum eucalypti** (*Oil of Eucalyptus*). Colourless or faintly yellow liquid containing at least 50 per cent. by volume cineol;  $d_{25^{\circ}}$  0,905 to 0,925; soluble in every proportion in alcohol; soluble in 3 volumes 70 per cent. alcohol;  $\alpha_{D25^{\circ}}$  not higher than  $+10^{\circ}$ ; free from phellandrene.

**Oleum foeniculi** (*Oil of Fennel*). Colourless or faintly yellow;  $d_{25^{\circ}}$  0,953 to 0,973; soluble in an equal volume alcohol, and also in 10 volumes or less 80 per cent. alcohol; congealing point not below  $5^{\circ}$ .

**Oleum gaultheriae** (*Oil of Gaultheria*). Colourless or almost colourless;  $d_{25^{\circ}}$  1,172 to 1,180; boiling point  $218^{\circ}$  to  $221^{\circ}$ ; feeble lævorotation up to  $-1^{\circ}$  in a 100 mm. tube at  $25^{\circ}$  C.

**Oleum hedeomae** (*Oil of Hedeoma*). Faintly yellow;  $d_{25^{\circ}}$  0,920 to 0,935; forms a clear solution with 2 or more volumes 70 per cent. alcohol;  $\alpha_{D25^{\circ}}$  from about  $+18^{\circ}$  to  $+22^{\circ}$ .

**Oleum juniperi** (*Oil of Juniper*). Colourless, faintly green, or yellow;  $d_{25^{\circ}}$  0,860 to 0,880; soluble in 10 volumes 90 per cent. alcohol.

**Oleum lavandulae florum** (*Oil of Lavender Flowers*). Colourless or yellow;  $d_{25^{\circ}}$  0,880 to 0,892; soluble in 3 volumes 70 per cent. alcohol.

**Oleum limonis** (*Oil of Lemon*). Faintly yellow liquid, containing not less than  $4\frac{0}{10}$  aldehyde, calculated as citral;  $d_{25^{\circ}}$  0,851 to 0,855;  $\alpha_{D25^{\circ}}$  not below  $+60$ ;  $\alpha_D$  of the first  $10\frac{0}{10}$  of the distillate may not differ more than  $2^{\circ}$  from the angle of rotation of the oil.

**Oleum menthae piperitae** (*Oil of Peppermint*). Colourless oil containing not less than  $8\frac{0}{10}$  ester (calculated as menthyl acetate) and  $50\frac{0}{10}$  total menthol (free and as ester);  $d_{25^{\circ}}$  0,894 to 0,914; forms a clear solution with an equal volume alcohol; the solution in 4 volumes 70 per cent. alcohol may show at most a feeble opalescence;  $\alpha_{D25^{\circ}}$   $-25^{\circ}$  to  $-33^{\circ}$ .

**Oleum menthae viridis** (*Oil of Spearmint*). Colourless, yellow, or greenish yellow;  $d_{25^{\circ}}$  0,914 to 0,934; with an equal volume 80 per cent. alcohol it forms a clear solution which becomes cloudy when further diluted;  $\alpha_{D25^{\circ}}$   $-35^{\circ}$  to  $-48^{\circ}$ .

**Oleum myristicae** (*Oil of Myristica*). Colourless or faintly yellow;  $d_{25^{\circ}}$  0,862 to 0,910; soluble in an equal volume alcohol, and in 3 volumes 90 per cent. alcohol;  $\alpha_{D25^{\circ}}$   $+14^{\circ}$  to  $+28^{\circ}$ ; when 2 or 3 cc. oil are evaporated, no crystallising residue may remain behind.

**Oleum pimentae** (*Oil of Pimenta*). Colourless, yellow or reddish; contains at least 65 per cent. by volume eugenol;  $d_{25^{\circ}}$  1,033 to 1,048; miscible in every proportion with 90 per cent. alcohol; soluble in 2 volumes 70 per cent. alcohol.

**Oleum rosae** (*Oil of Rose*). Faintly yellowish oil with a saponification number not below 10 nor above 17;  $d_{25^{\circ}}$  0,855 to 0,865; congealing point between  $18^{\circ}$  and  $22^{\circ}$ .

**Oleum rosmarini** (*Oil of Rosemary*). Colourless or faintly yellow; it must contain at least 5 % ester (calculated as bornyl acetate) and 15 % total borneol;  $d_{25^{\circ}}$  0,894 to 0,912;  $\alpha_{D25^{\circ}}$  not above  $+15^{\circ}$ ; the first 10 % of the distillate must also be dextrorotatory; soluble in one half and more vol. 90 per cent. alcohol, and in 2 to 10 volumes 80 per cent. alcohol.

**Oleum sabinae** (*Oil of Savin*). Colourless or yellowish;  $d_{25^{\circ}}$  0,903 to 0,923;  $\alpha_{D25^{\circ}}$   $+40^{\circ}$  to  $+60^{\circ}$ ; soluble in about one half and more volumes 90 per cent. alcohol.

**Oleum santali** (*Oil of Santal*). Faintly yellow oil with a content of at least 90 % santalol;  $d_{25^{\circ}}$  0,965 to 0,975;  $\alpha_{D25^{\circ}}$  between  $-16^{\circ}$  and  $-20^{\circ}$ ; soluble in 5 volumes 70 per cent. alcohol.

**Oleum sassafras** (*Oil of Sassafras*). Yellow or reddish yellow;  $d_{25^{\circ}}$  1,065 to 1,075;  $\alpha_{D25^{\circ}}$  not above  $+4^{\circ}$ ; soluble in every proportion in 90 per cent. alcohol.

**Oleum sinapis volatile** (*Volatile Oil of Mustard*). Colourless or faintly yellow oil, containing at least 92 % allylisulphocyanic acid ester;  $d_{25^{\circ}}$  1,013 to 1,020; forms a clear mixture with alcohol in every proportion; boiling point  $148^{\circ}$  to  $152^{\circ}$ .

**Oleum terebinthinae** (*Oil of Turpentine*). Colourless oil;  $d_{25^{\circ}}$  0,860 to 0,870; on distillation the bulk must pass over between  $155^{\circ}$  to  $162^{\circ}$ ; soluble in 3 volumes alcohol.

**Oleum terebinthinae rectificatum** (*Rectified oil of Turpentine*). Colourless;  $d_{25^{\circ}}$  0,860 to 0,865.

**Oleum thymi** (*Oil of Thyme*). Colourless oil, containing at least 20 per cent. by volume phenols;  $d_{25^{\circ}}$  0,900 to 0,930; feeble lævo-rotation;  $\alpha_{D25^{\circ}}$  not above  $-3^{\circ}$ ; soluble in one half vol. alcohol, and in 1 to 2 volumes 80 per cent. alcohol.

**Safrolum** (*Safrol*). Colourless or faintly yellow;  $d_{25^{\circ}}$  1,105 to 1,106; boiling point about  $233^{\circ}$ ; optically inactive; when cooled down to  $-20^{\circ}$  or below, it congeals into a crystalline mass, which does not melt below  $11^{\circ}$ ; soluble in about an equal volume strong alcohol, and in about 30 volumes 70 per cent. alcohol.

**Terebenum** (*Terebene*). Colourless liquid, consisting of dipentene and other hydrocarbons;  $d_{25}^{\circ}$  about 0,850; boiling point  $155^{\circ}$  to  $165^{\circ}$ ; soluble in 3 volumes alcohol.

**Thymol**. Large, colourless, transparent rhombic prisms;  $d_{25}^{\circ}$  1,030; melting point  $50^{\circ}$  to  $51^{\circ}$ ; the alcoholic solution is optically inactive.

**Vanillin**. Fine, white, crystalline needles; soluble in about 100 parts water of  $25^{\circ}$ , and in 15 parts of  $80^{\circ}$ ; readily soluble in alcohol; melting point  $80^{\circ}$  to  $81^{\circ}$ .

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### On the distillation of liquids which do not dissolve each other.

In our Report of April 1904, p. 102, we referred to researches made by E. Charabot and J. Rocherolles<sup>1)</sup> on the relative quantities of the individual constituents of a vapour-mixture which is obtained by introducing water vapour into a volatile liquid not miscible with water, when this liquid is heated indirectly above its boiling point in the mixture with water.

On the strength of three distillation tests, in which they passed water vapour through rectified turpentine oil at reduced pressure, the authors had drawn up the proposition, that in this case, of the mixture of vapours rising from the oil, the oil vapour has the pressure corresponding to the temperature of the vapour-mixture, and the water vapour the pressure to which the oil is subjected in the distillation-vessel.

The formula was:

$$P : P_1 = M\varphi : M_1 h,$$

in which  $P$  represents the quantity by weight of the essential oil distilling over in the unit of time, and  $P_1$  that of the water;  $M$  and  $M_1$  the molecular weights of the 2 liquids;  $\varphi$  the vapour-pressure of the oil corresponding to the temperature of the vapour-mixture, and finally  $h$  the vapour-pressure of the water, which, as the authors maintain, is equal to the total pressure existing in the distillation-vessel.

This statement is erroneous, as will be found on due consideration, and as the experiments made by us have also proved.

With regard to the distillation of mixtures of liquids, i. e. of such liquids which do not dissolve each other, we know from Magnus and Regnault that each of the liquids of which the mixture consists, develops vapour without being influenced by the vapour of the other liquid. Their vapour-pressure is the same as if each were heated by itself to the temperature in question. Now, as generally speaking

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<sup>1)</sup> Compt. rend. **138** (1904), 497; Bull. Soc. Chim. III. **31** (1904), 533.

a liquid boils when its vapour pressure has reached the external pressure exerted on the liquid, the boiling point of mixtures of liquids is already reached when the sum of the vapour-pressures of the liquids of which the mixture consists, is equal to the external pressure.

The investigations of Gay-Lussac, Wanklyn, Berthelot and A. Naumann have moreover established with regard to the vapour-mixture rising from the mixture of liquids, that the volumes of vapour of the two substances in the vapour-mixture are proportional to their vapour-pressures at the temperature of the vapour mixture; or the weights of the vapours, to the products of the vapour-pressures with the molecular weight.

In this respect the knowledge as to the relative quantities in the vapour-mixture is laid down theoretically, but only for saturated vapours, and not for a mixture of vapours of which one constituent is saturated, and the other unsaturated. Such a case presents itself in the distillation method used by Charabot and Rocherolles for their investigation.

The oil vapour occurs in the vapour-mixture in a saturated condition; the water vapour, on the other hand, is superheated by the oil. For the oil vapour it is therefore necessary, in order to calculate its quantity, to determine the pressure which corresponds to the temperature in question of the vapour-mixture. But the pressure of the superheated water vapour is not at once known; it can, however, be calculated, by taking into consideration that, jointly with the oil vapour, it represents the total pressure of the mixture of vapours; it is consequently obtained as the difference between the vapour-pressure of the oil, and the external pressure.

For the rest, the method of distillation just discussed represents but one of many distillation possibilities with formation of partially saturated vapour-mixtures.

As a matter of fact, in the essential oil industry there are usually obtained only partially saturated vapour-mixtures, but with this difference, that then the oil vapour is unsaturated.

If a vegetable material which contains substances volatile with vapour is distilled either when immersed in the water, by boiling the water, or without the addition of water, by passing water vapour through it, the vapour mixture passing into the condenser is, with few exceptions, saturated in its water content, in its oil content unsaturated, superheated.

The same takes place when an essential oil is boiled with water for the purpose of rectifying or fractionating the oil, in case the oil layer is inconsiderable, and especially if the distillation is violent.

As a proof of the correctness of our view that it is in all these cases a question of vapour mixtures with a saturated and a superheated constituent, the following experience may still be quoted.

If a completely saturated vapour-mixture is only partly cooled, the condensed substance separated off contains oil and water in the same proportion as in the vapour-mixture. If, on the other hand, a partially unsaturated vapour-mixture is cooled, there separates off at first either nothing but water, or only oil, according as either the one or the other constituent was saturated in the vapour-mixture; for instance, only oil in the distillation method in which the water vapour passes through the oil heated to above the boiling point of water and oil combined.

In the case of this last-named method of distillation it may easily happen that the vapour-mixture is unsaturated in both its constituents, when, of course, a calculation of the proportionate quantities in the vapour-mixture is out of the question. The water vapour is forced too rapidly and in too large bubbles through the oil, especially in the case of distillation *in vacuo*, as employed by Charabot and Rocherolles. If to this is added a still greater difference in temperatures between the water vapour rushing into the oil, and the oil itself, it is clear that even in the slowest distillation, there can never be a perfect, but at most only an approximately complete intermixing of the oil and the water.

In this appears to us to lie the principal cause of the erroneous observation-results of the above named authors.

The calculation of the proportionate quantities in the vapour-mixture was made in the experiments quoted below according to the formulae:

$$g : g_1 = Mp : M_1 (P - p)$$

for a vapour-mixture in which the water vapour is unsaturated, and

$$g : g_1 = M (P - p_1) : M_1 p_1$$

for a vapour-mixture with unsaturated vapour of the essential oil.

Here represent:  $g$  and  $g_1$  the weights of the essential oil and the water;  $M$  and  $M_1$  the respective molecular weights;  $p$  the vapour pressure of the essential oil in the vapour mixture;  $p_1$  that of the water, and  $P$  the pressure of the vapour-mixture.

When using our letters, the formula for unsaturated water vapour in the vapour-mixture according to Charabot and Rocherolles would read:

$$g : g_1 = Mp : M_1 P.$$

Distillation experiments with unsaturated water vapour in the vapour mixture.

1. Distillation at atmospheric pressure. The middle fraction of turpentine oil was heated in the still by passing steam through the

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Miltitz near Leipzig, October 1901.

Since the publication of our last Report, important changes in the economic condition of Germany have been developing, changes which are casting their shadows ahead, and are making their influence felt on the general state of affairs.

In the front rank appear the new Customs Tariff and the Commercial Treaties with other countries. This is not the place to express an opinion as to whether, and in how far, the Government's project of the new Customs Tariff is acceptable. Nowadays the interests of all the more important branches of Trade and Industry are represented much more powerfully by special organs, than is possible even by the Chambers of Commerce, whose province it is. The former display at present such great activity, and offer to every individual the opportunity to ventilate his views and his desires, that it does not seem opportune to continue in Reports like the present one, the already excited controversy, and perhaps render it more acute. With regard to our own line, after exertions extending over several decades, the general desire to exempt the various seeds, such as anise, coriander, fennel and caraway, which are used in the manufacture, has at last been taken into consideration. It is proposed to admit these seeds in future free of duty for the distillation of essential oil, subject to an official permit and control. But in order to render this concession of real value to our industry, it is necessary that the residues of the distillation should be left to the manufacturer and not (as is the case with spices) that they should be required to be destroyed. These residues namely are dried, and form a valuable food for cattle. Successful competition with abroad is only possible if, in addition to the duty saved, these residues can be turned to account.

On the other hand, it cannot be denied that the essential oil may only partly be abstracted from these seeds, and that the latter may be subsequently dried, with the view of using them dishonestly for mixing with normal qualities of seed.

For this reason it is necessary to grind or crush these seeds before the distillation; they should, moreover, be completely exhausted in the distillation process, so that it may be possible to exempt them from duty when worked up into food for cattle.

We have no doubt that the proposals made by us, which meet both cases, will be accepted, and that this contentious point may thereby be settled once for all.

But, as nothing has been inserted in the draft Tariff without a *quid pro quo*, the import duty on the seeds mentioned above — in so far as those seeds are not used for the preparation of essential oils — has been raised from 3 Marks to 4 Marks per 100 kilos, and that on essential oils from 20 Marks to 30 Marks per 100 kilos. The last-named increase is not only injurious to the German middleman, but has also the effect of raising the price of a large number of foreign essential oils which are indispensable for the home manufacture of perfumes and soaps.

The imports of foreign essential oils amounted in 1900 to  
420,900 kilos, value Marks 5,631,000.—

The exports on the other hand, came to

386,200 kilos, value Marks 4,634,000.—

against:—

in 1899:	351,100	"	"	"	3,862,000.—
" 1898:	287,100	"	"	"	2,871,000.—
" 1897:	271,500	"	"	"	2,987,000.—

The exports of German perfumes and toilet soaps in 1900, are made up as follows:—

	kilos		value
Soap in tablets, including scented soap	3,922,400	M.	5,491,000.—
Fatty oils, scented . . . . .	7,100	"	82,000.—
Scents, not containing alcohol . . . . .	11,400	"	11,000.—
Liquid perfumes, containing alcohol or ether, including hair-washes, dentrifices, and mouth-washes . . . . .	1,477,400	"	7,387,000.—
All other perfumes not otherwise enumerated . . . . .	590,300	"	2,066,000.—
Soap and perfumes, insufficiently specified	2,800	"	11,000.—

Total: kilos 6,011,400 M. 15,048,000,—

against which the values of the exports were:—

in 1899	Marks	15,415,000
" 1898	"	12,972,000
" 1897	"	11,714,000
" 1896	"	12,549,000,

showing a very slight decrease only as compared with 1899.

It is already evident by the important increase in the figures of the export of essential oils, that the export of our manufactures is slowly but constantly growing. The trade with the United States was fairly brisk, and will, it is hoped, not be influenced by the tragic fate which has befallen President Mac Kinley, who was the object of universal sympathy. The conditions in Cuba and the Philippines are visibly improving. With regard to South America, the situation in Brazil, Colombia and Venezuela is very unfavourable. In the Argentine Republic and Chile an improvement in the economic conditions seems to be approaching; on the other hand, the conditions in Mexico have developed into a general commercial crisis. Trade with Japan and the Dutch Indies was fairly brisk during the last half year; also that with Australia, partly direct, partly via London. In several European countries a certain economic stagnation has set in, which, after the general excessive pressure, was inevitable. Another factor, exerting a somewhat paralysing influence on the spirit of enterprise, is the uncertainty as to the fate of the new commercial treaties. Nevertheless, the conviction that the peace of the world is assured for some time to come, coupled with the fall in the price of coal, will give the German Industry confidence and strength to overcome the crisis.

Our town and the lesser fatherland Saxony have suffered a terrible blow by the collapse of the time-honoured Leipzig Bank, a blow which has destroyed many an existence, and has caused nameless misery. The persons appointed to the management of this institution have, in the most irresponsible manner, administered and speculated with money not their own, attracted by the fatal passion for rapid gain, by insensate ambition, and a mania for greatness. However disastrous the consequences of this catastrophe are, and still will be, it may be hoped that it will serve as a warning, a memento mori, to many banking institutions, and that it may bring about a discontinuance of the company-promoting scandal which had reached the highest point of development. Many banks and industrial firms suffer from an abundance of unrealisable assets, with which the public have often been deluded for many years. May the investing public draw a lasting lesson from this collapse.

The state of the weather during the past summer has been favourable in most countries which produce materials for our industry; as a consequence a backward tendency in the prices predominates.

The activity during the last six months in the domain of Science has had beneficial results, and offers abundant material for report.

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The transfer of our business to the new premises, described in our last Report, has taken place on the 1<sup>st</sup> May of this year.

All the various arrangements, based as they are upon the widest experience, have proved most excellent, and answer throughout the most modern requirements. The despatch of goods to be forwarded especially works faultlessly, as all possibility of delay in cartage to the station, which is unavoidable in a large town, is now prevented by our deliveries direct into the corresponding train.

With regard to the general conduct of our business, we would mention here, for practical reasons, that all orders received by first post are executed the same day. Orders by telegraph which reach us before 5 p. m. are, if at all possible, sent off the same evening.

Telegrams should be addressed thus:—

**Schimmel, Miltitz-Leipzig,**

Miltitz-Leipzig having its own independent telegraph office.

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**Almond Oil, pressed from apricot kernels.** The following original reports have come to hand on this year's harvest of apricot kernels in Syria:—

#### Damascus.

Damascus stands in the front rank both as regards quantity and quality. Early in 1900 some 600 to 700 bales of the 1899 harvest were still shipped from there; at the commencement of the new harvest there was nothing, or perhaps only a very small quantity, of the old stock left. The yield in 1900 was very small; the estimate of about 1500 bales has proved correct. Of these, about 1000 to 1100 bales were shipped at the end of 1900, and the remainder this year; since June there has been nothing on the market. In consequence of the small harvest the price was very high, but in the spring of 1901 the quotations dropped, in view of the favourable prospects of the new harvest. There were also complaints in Europe about bad trade in the branches which chiefly consume kernels.

During the months from May until August the demand was brisk, especially from Italy, but it could only partly be satisfied. At that time Italy already placed orders for kernels of the new harvest at Fr. 67.— to 68.— c.i.f. Genoa. The Damascus harvest of this year has turned out very satisfactory. The estimates fluctuate between 4000 and 6000 bales; the truth lies probably in the middle.

Owing to pressing purchases the prices opened at Fr. 70.— to 72.—, but they soon receded, and in October they will probably be a few francs lower still.

Besides Damascus, there are still the undermentioned sources from which a less valuable product is obtained, which is bought

chiefly by Trieste, Marseilles, Italy and Hamburg, at Fr. 5.— to 7.—, below the Damascus rates.

### Tripoli.

The supplies from here both in 1900 and 1901 have averaged 250 bales. These kernels can already be shipped in July, but they lose during transport about 3 to 4 per cent in weight, because they are so fresh. This year the kernels have partly been bought firm and too dear by Italy, and partly been consigned to Hamburg, where they can only be sold at much below cost price.

### Aleppo (port of shipment: Alexandrette).

It is difficult to check the export, but it does probably not exceed a few hundred bales.

### Mersina

supplied some 150 to 180 bales from the plain of Tarsus, and about 600 bales from Konia and Cesarea.

The 150 to 180 bales have been bought this year by Trieste and Italy; these kernels also lose about 3 to 4 per cent in weight, as they are shipped quite fresh.

The Konia and Cesarea kernels are drier, but of somewhat less value than those from Tarsus; there are always a good many rancid kernels among them. The yield from the plain of Tarsus in the years 1900 and 1901 was about the same; that of this year in Konia and Cesarea is as yet unknown.

The favourable results of the harvest mentioned above have, naturally, not remained without effect on the prices of the products obtained from apricot kernels.

The strong demand for pressed almond oil compelled us to carry on the manufacture with great activity, in consequence of which large quantities of essential oil of bitter almonds were also obtained, which caused a decline in the price. Our purchases of 1901 kernels have been so advantageous, that our quotations of both products could again be reduced.

As the following statistics show, the prices of pressed oil are lower now than they have been for several years; it is therefore recommended to lay in an ample supply:—

Quotations of almond oil, pressed from apricot kernels.

On 1 <sup>st</sup>	October	1894 . . . .	Marks	130.—
„ 1 <sup>st</sup>	„	1895 . . . .	„	135.—
„ 1 <sup>st</sup>	„	1896 . . . .	„	170.—
„ 1 <sup>st</sup>	„	1897 . . . .	„	160.—
„ 1 <sup>st</sup>	„	1898 . . . .	„	145.—
„ 1 <sup>st</sup>	„	1899 . . . .	„	145.—
„ 1 <sup>st</sup>	„	1900 . . . .	„	155.—
„ 1 <sup>st</sup>	„	1901 . . . .	„	140.—

**Almond Oil, pressed from sweet almonds, Ph. G. IV.** The unprecedented high prices of this article, which had been maintained during the last few years, have at last dropped, in consequence of rich harvests in Sicily and in Puglia, and although the present quotation cannot yet be called normal, it rests upon a reasonable basis. We are, however, firmly of opinion that in the course of the season the price will experience a further drop, and would for the present advise abstention from large transactions in almond oil.

**Angelica Oil.** The yield of our own crop, like that in the Erzgebirge and in Thuringia, is a very small one. Under the influence of the drought the plants have developed but poorly.

As a consequence high prices are again probable this year, both for roots and for the essential oil.

**Anise Oil.** With regard to this year's anise harvest in Russia, we hear from a reliable source, that anise has been sown on an area equal to about three quarters of that of last year, but a yield proportionate in quantity is not expected; in fact, the estimate does not exceed one-half of last year's crop. The continued drought which prevailed this summer in Russia, threatened the seed sown for a time with total destruction, but at the eleventh hour a rainfall over the greater part of the area under cultivation fortunately removed the threatening danger. Only here and there, in places where no rain has fallen, the seed which had begun to grow has withered completely, and even the subsequent rain has not been able to make good the damage done.

From other sides the yield is estimated as rather below the medium. They also are of opinion that the area under cultivation is considerably smaller than that of 1899. In the Southern Districts the plants have developed better than in the North, where, owing to want of rain, many plants are completely shrivelled up. The yield is estimated as at most 3,000,000 kilos, against 4,000,000 in 1899.

The total result of this year's harvest is in any case but middling; the quality, however, is excellent, better than in 1900.

At the first Russian anise market the supply was very small, owing to the incessant rain, whilst prices ruled so high that there was very little inclination to buy. We think there can be no doubt that the quotations of anise oil, made from this year's seed, will experience a considerable rise.

No reports have so far reached us with reference to the results of the anise harvest in other countries. But they could have no influence on the prices of anise oil, for the other sorts are exclusively commercial qualities, and, owing to their pure character, are better suited for that purpose than the Russian seed which is always more or less mixed with earth.

The production of aniseed in Spain is very considerable. Alicante alone exported in 1900, 531,555 kilos.

Important transactions in last year's aniseed enable us, for some short time yet, to disregard the present state of the article, and our low quotations, both of anise oil and of our speciality "anethol", will remain in force until further notice.

**Anethol.** The fact that anethol has been inserted in the fourth edition of the German Pharmacopœia in lieu of anise oil, is no doubt to be considered as a step in advance. True, the German Pharmacopœia does not refer to the optical behaviour of anethol, but the latter must unquestionably be optically inactive. The slightest deviation of the plane of polarised light either to one side or to the other, points to an insufficient degree of purity in the preparation under examination. A communication from Pancoast and Kebler on anise oil and anethol<sup>1)</sup> shows, however, that such impure preparations are still frequently met with in the trade. The authors publish in that article *inter alia* the physical constants found by them for some samples of anethol. These are all characterised by an exceedingly low congealing point; moreover, they are partly optically active, and distil within a wide range of temperatures, as, for example, two samples between 210 and 235°. As the authors express the opinion that some of the specimens examined are good preparations of anethol, we would point out that this can hardly be the case, but that, on the contrary, the preparations must either have been adulterated, or simply have been prepared by fractional distillation from anise oil.

With regard to the congealing point, we have repeatedly called attention to the fact, that prolonged unsuitable storage of anethol causes the formation of products of oxidation, which lower the congealing point, and which finally make crystallisation quite impossible. On the other hand, the congealing point is frequently found a little too low, because the specimen had been cooled too much during examination. It may be recommended that the cooling should not be carried below 5°, as otherwise the congealing point might be found considerably lower than the melting point, whereas these two should be situated as close together as possible.

The congealing point of our freshly prepared anethol is always at 21° and over, whilst the melting point lies between 22.5 and 22.7°. Others give the melting point of anethol as 22°, so that our preparations are still superior to those.

**Bay Oil.** We now distil this oil at our Works on the largest scale, from material imported by us direct, and supply it in all quantities. The consumption of bay rum has been large, owing to the exceptionally hot summer. This pleasant hair-wash, to which

<sup>1)</sup> Americ. Journ. Pharm. 73 (1901), 356.

we made the first reference in our Report of 1878, is now used all over Europe, following the American example, and it has become an article of considerable importance for the perfumery trade.

With the view of meeting a demand which has frequently been brought before us, we now also supply a readily soluble, extra strong bay oil, which is distinguished by its high phenol-content, and of which the physical constants are approximately as follows:—

Specific gravity at 15° = 1.04

Optical rotation = — 0° 10'.

With 3 or more volumes of 60 per cent alcohol the oil makes clear solutions, and it may therefore be taken as satisfying the most far-reaching requirements.

In cases, however, where ready solubility is not absolutely essential, we recommend that the usual distillate should be given preference, as the extra strong oil does not contain certain constituents which have a decided influence on the aroma of bay oil.

We would here again call attention to the fact that the solubility of common bay oil gradually diminishes, owing to the polymerisation of the terpene "myrcene" contained in it.

**Calamus Oil.** The dry summer has greatly facilitated the cutting of the calamus roots in the ditches of our neighbourhood, and as a consequence comparatively large quantities of material were once more, after many years, available for distillation. For this reason, little attention was paid to numerous offers of whole truck-loads from East Prussia and Galicia. A consignment of Japanese rhizomes, which yield the well-known readily soluble oil, is in course of shipment to our Works.

Some time ago<sup>1)</sup> we detected in calamus oil a compound melting at 167°, which undoubtedly is identical with a body of the formula  $C_{15}H_{26}O_2$  found subsequently by H. v. Soden and W. Rojahn<sup>2)</sup> in Galician calamus oil.

Recently H. Thoms and R. Beckstroem<sup>3)</sup> have published a communication on the constituents of calamus oil.

They examined a fraction of oil originating from our factory and found in it, — in addition to free fatty acids, eugenol and oxygenated bodies which are still to be further identified, — also the compound mentioned above, which separated out from the highest boiling portions of the fraction, after standing for a considerable time, and which, after repeated recrystallisation from alcohol, showed a melting point of 166—167.5°. Elementary analysis and determination of molecular weight gave figures corresponding to the

<sup>1)</sup> Report October 1899, 8.

<sup>2)</sup> Pharm. Ztg. 46 (1901), 243.

<sup>3)</sup> Berliner Berichte 34 (1901), 1021.

formula  $C_{15}H_{26}O_2$ . At the present moment the authors are still engaged on a more detailed examination of this compound.

Thoms and Beckstroem further obtained from the mother liquor of the crystals, an abundant quantity of a second well-crystallising substance, which melted at  $61^{\circ}$ , and which was found to be asarone. This substance had so far only been found in the oil of *Asarum europaeum* L. and in matico oil, and its detection in calamus oil is especially interesting for this reason, that according to Thoms and Beckstroem asarone is connected with the fragrant principle of calamus oil.

The authors, namely, by shaking the fraction of calamus oil with a solution of sodium bisulphite, and by suitable further treatment of the bisulphite compound thus obtained, isolated an oil at first colourless, but soon changing to yellow, which is believed to be connected in a pronounced manner with the characteristic odour of calamus oil, but which could not be obtained pure for analytical purposes. While being kept, crystals were formed, the odour of the oil meanwhile disappearing. The crystals were found to be asaryl aldehyde, which was proved also by the oxime obtained from it.

The authors are engaged on further experiments to detect the connection between asarone and the peculiar odoriferous body of calamus oil.

**Camphor Oil.** An important change in this Japanese product is highly probable in the near future. The Japanese Government, encouraged by the results of the camphor monopoly, has given notice of its intention to stop the sale of camphor oil altogether, and to undertake itself the working up of the oil into its different constituents.

According to the following article abstracted from the *Osaka Mainicki* of 25<sup>th</sup> June 1901, the factory in which this work is to take place, is already in operation!

This article, translated literally, reads as follows:—

“The day before yesterday Dr. Shimoyama inspected the safrol factory of the Formosa Camphor Departement, at the moment when the Minister of War, Baron Kodama, also paid a visit to those works.

Dr. Shimoyama, the inventor of the new chemicals “Desinfectol” and “Insectol” says:—

White and brown camphor oil are by-products of the camphor manufacture. The white oil is used in Japan for preparing paints and varnish, and is also exported; the brown oil, however, was unknown in Japan, and was considered valueless, until about 1879–1880, when Mr. Goto Katsuzo commenced to export it, since when he has continued to ship it to Messrs. Schimmel & Co. in Germany. As we now use it ourselves in Japan, the export of the brown camphor oil made at the Formosa camphor factories, will be discontinued. In the year 1884, when I was a student in Germany, my teacher Dr. Krieger, one of the most capable chemists of the time, showed me a Report of Messrs. Schimmel & Co., in which it was stated that Dr. Bertram, the chemist of that firm, had detected safrol in brown camphor oil; and he told me that

the study of such a subject was a matter for Japanese students. At that time I did not dream that I would one day be the inventor (*sic*). In February last year, when I was in Formosa for the purpose of making scientific researches, I received instructions from the authorities to find a method for the manufacture of safrol from brown camphor oil. Under my supervision a large factory was erected at Kobe. The quality of the safrol made there is not inferior to, perhaps better, than that made by Schimmel & Co., as is shown by the specific gravity. The recently discovered chemicals "Desinfectol" and "Insectol" are by-products of safrol. "Desinfectol" has the property of destroying bacilli, and of disinfecting; it is, moreover, a deodorizer, and cleans substances better than soap does. After the most careful experiments, the following conclusions were arrived at by Dr. Kitasato, in his Institute for infectious diseases: Desinfectol diluted with 200 parts water destroys the bacillus of typhus and cholera in 5 minutes; when diluted with 100 parts water, it kills the bacilli of the large intestine, and the plague bacillus, also in 5 minutes. Diluted with 20 parts water it destroys in 40 minutes all bacilli found in excrements. This chemical product is therefore not only adapted to disinfection and the cleaning of bedding, cloths for breeding silk-worms, barbers' towels, &c., but also for cleaning clothing and other objects stained with oil, as it has the property of removing oil stains.

With regard to "Insectol", this has the effect of killing insects, whilst at the same time it is perfectly harmless for plants and for the human body. It will prove very useful especially for agricultural purposes."

If this information should be correct, the export of camphor oil will probably soon come to an end; fortunately, however, we are not unprepared for such a sensational change, as we have a large quantity in stock, which enables us to supply our clients for many years to come, in the most liberal manner, with the products of camphor oil. It will soon be known whether the Japanese Government actually realizes the hoped-for profit, or whether it has not largely over-estimated the consumption of safrol. In our opinion the working up of camphor oil, as an independent industry, can never be made to pay. Our own firm has declined to take up the sale of the production of the Japanese factory.

In the two by-products "Desinfectol" and "Insectol" it may be possible to recognise two old friends, viz., light and heavy camphor oil. As, however, neither is soluble in water, the information given above as to the dilution of the former with water needs scarcely be taken seriously.

Our removal to the new premises has caused repeated stoppages in the production of light camphor oil, in consequence of which we have not always been able to supply this fraction in large parcels. This calamity will unfortunately last for some time longer; and later on the price will also be so high, that it is questionable whether this article will still find such a large application as hitherto.

Heavy camphor oil is always in stock in quantities.

We have abstracted the following from an article in the *Journal d'Agriculture tropicale* of this year, p. 44, headed: "*Le problème de la culture commerciale du camphre.*"

As the monopolising of the Formosa camphor by the Japanese Government has exerted a pronounced influence on the world's trade in this product, and as the European industry has now for some years consumed more camphor than ever, the question of the cultivation of the camphor tree has been seriously considered in several botanical gardens in the tropics. This tree has become almost as common in tropical climates as in the countries of the temperate zone; it is, for example, found in great numbers in California and Australia, and according to Naudin (*Manuel de l'acclimateur*, 1887) it has been introduced long ago in the Basse-Provence, where it is not affected even by slight frost. In all these countries the camphor tree has for the present a purely decorative character; at least there is no record of any results obtained with the cultivation of this tree. Mr. Willis, the director of the Botanical garden in Ceylon, has, however, held out a prospect of such particulars; for this purpose he has sent a form of enquiry to every planter in Ceylon who has attempted the cultivation of the camphor tree.

In the meantime professor Trabut, director of the Botanical garden at Algiers, has found, in examining the branches of a number of camphor trees, that whilst some of these only contained traces of camphor, others yielded as much as 0.5, or even 1 per cent. From this it may be concluded, that for a remunerative cultivation of the camphor tree, it will be necessary to select the plants most carefully, in the same manner as is done with the various kinds of cinchona trees, and with the trees supplying india rubber.

**Caraway Oil.** The situation of this important article has again become favourable.

We have received the following report from a perfectly competent correspondent in Holland (which is the principal producing country):—

“During the spring the weather-conditions were very favourable for the plants, but the summer was too dry, owing to which the plants remained small, and the result of the harvest was slightly below what had been anticipated. The area cultivated with caraway was, however, very large. The figures for the different provinces were approximately as follows:—

North Holland . . . . .	about 3700 acres
Zeeland . . . . .	„ 2500 „
North Brabant . . . . .	„ 2500 „
South Holland . . . . .	„ 250 „
Friesland . . . . .	„ 250 „
Groningen . . . . .	„ 250 „

Total about 9450 acres.

Taking the average yield at 12 bales of 50 kilos per acre, the new crop would roughly amount to 114,000 bales, to which may be added some 15,000 bales of old seed from different previous harvests.

Of the first named quantity a good proportion has already changed hands, partly for direct shipment, partly for purposes of speculation, but about one half is probably still unsold.”

The prices have naturally moved in harmony with the rich crop. The lowest quotation of common average quality was about Fl. 11.— per 50 kilos; that of seed from favoured situations Fl. 11.50 per 50 kilos, prices such as we cannot recall to our mind.

With regard to the oil-content, the Dutch seed has been on the downward move for several years. This fact is thought not to be unconnected with the constantly growing method of manuring the fields with Chile saltpetre.

In face of these low quotations the position of the other caraway producing countries is rather difficult. The yield of this year's harvest in Sweden and Norway cannot yet be estimated. But whether it be large or small, the prices will have to follow those of the Dutch seed, and the same applies to the East Prussian caraway, in spite of the slow manner in which offers made to those countries have been treated.

We have so far purchased about 3000 bales of the finest Dutch seed, at the lowest current prices, and have now finally fixed our quotations of caraway oil and carvol. The large increase in the consumption of carvol causes an accumulation of comparatively large quantities of carvene — the light portion of caraway oil — which we sell at exceptionally low prices. In the manufacture of cheap soap this body is an excellent substitute for caraway oil, and it is already used as such to a considerable extent.

Some years ago Kremers and Schreiner recommended a method for the quantitative estimation of carvone in the oils containing this ketone, by which the carvone was converted into carvoxime, and was weighed in that state. In our Report of October 1896, page 17, we called attention to some defects in this method of examination, whereupon professor Kremers had a number of experiments made in his laboratory, in order to determine the most favourable conditions for obtaining exact and corresponding results (compare our Report of October 1899, page 12). Since then the examinations have been continued; and in a recently published work<sup>1)</sup>, to which we would here draw attention, the learned professor discusses in detail the steps to be taken so as to reduce the errors as much as possible.

At the end of his summary the author says (and we quite agree with him): "Although the method of determining the carvone as carvoxime may not by any means be perfect, it is unquestionably a step in the right direction. The one great advantage in the method proposed is, that the analyst weighs a definite crystalline compound."

**Cardamom Oil.** The Ceylon cardamom oil mentioned in our price-lists is no longer made by us from the fruits of *Elettaria Cardamomum* var.  $\beta$ , but is now distilled from the seeds of another

<sup>1)</sup> Journal of the Soc. of Chem. Industr. 20 (1901), 16.

species from which the pericarp has been removed. As the seed is shipped from Ceylon under the name of "cardamom seeds", the designation "Ceylon cardamom oil" is quite justified for this oil. It differs, however, from the oil previously supplied by us; according to various determinations our present Ceylon cardamom oil has approximately the following constants: specific gravity at 15°, 0.9336; optical rotation +24° 15'; saponification number 109. The oil makes a clear solution with 3 parts by volume of 70 per cent alcohol.

**Cassia Oil, Chinese.** Since our last Report the prices in China have still further declined, and all attempts which have been made there from time to time to raise the quotations, have been unsuccessful. The decline is represented by the following comparative figures:—

	October 1900.	March 1901.	September 1901.
60—65 per cent aldehyde	37 d.	32 d.	29 d.
65—70 " " "	39 "	34 "	30 "
70—75 " " "	41 "	36 "	31 "
75—80 " " "	43 "	39 "	32 "
80—85 " " "	45 "	41 "	35 "

This is all the more surprising, as all reports speak of small stocks in China, the export figures also showing a considerable deficiency as compared with previous years. The consumption is normal. It is generally taken for granted that the decline of this article has now reached the extreme limit, and at the present quotations it seems a good speculative value.

**Cassia Oil, artificial, "Schimmel & Co."** This excellent product is quite unaffected by the movements in the value of the Chinese competitor; it holds an independent position, and has retained its old friends and gained new ones. Competition with the present prices of Chinese oil is absolutely out of the question, our quotations being calculated as low as possible.

**Cedarwood Oil.** Of the Atlas cedar oil, mentioned in our last Report, a sample consignment is at present on the way to our works from Algiers, where the manufacture has now been taken up on a large scale. This sample will reach us in a few weeks; the price will be about 24 Marks per kilo. We hope to be able to include it already in the next issue of our lists, and we will then have it examined to see whether its medicinal value equals that of East Indian sandalwood oil, as the manufacturer affirms.

**Champaca Oil.** A new consignment has recently arrived from Manila, which appears to have been produced by means of improved technical appliances, and which is of a higher quality than the previous product. The price is, moreover, lower.

**Cinnamon Oil, Ceylon.** Since the date of our last Report the price of fine cinnamon chips has undergone a further important reduction, and along with it also the quotation of the distillate, which we were the first to produce, now some 27 years ago. At that time the price of cinnamon chips was about 176 Marks per 100 kilos; now it is about 55 Marks; the imported oil cost then about 220 Marks, whilst its present quotation is about 70 Marks per kilo.

**Citronella Oil.** Contrary to all calculations the value of this leading article has gone back still further in the course of the last six months. It has now reached a level which would have been considered scarcely possible. This points to a considerable over-production of this oil also, an over-production which it is impossible to stem by ordinary means, and it will therefore be necessary to wait until this unhealthy state corrects itself. It will be remembered that already several years ago, when the price was 1/— per lb., the Ceylon papers described the distillation as wholly unremunerative, and shortly before the publication of our April Report we were informed from Galle, that in many districts in Ceylon the citronella cultivation had been entirely given up. If, in spite of this, the prices have declined about 20 per cent, this fact throws a very peculiar light on those statements.

The shipments from Colombo and Galle were as follows:—

From 1 <sup>st</sup> January to 1 <sup>st</sup> July 1901	634,608 lbs.
„ 1 <sup>st</sup> „ „ 1 <sup>st</sup> „ 1900	605,644 „
„ 1 <sup>st</sup> „ „ 1 <sup>st</sup> „ 1899	657,080 „
„ 1 <sup>st</sup> „ „ 1 <sup>st</sup> „ 1898	616,784 „

The first-named amount is made up as follows:—

United Kingdom . . . . .	374,007 lbs.
America . . . . .	138,749 „
Australia . . . . .	2,304 „
Germany . . . . .	110,373 „
France . . . . .	2,399 „
India . . . . .	174 „
China and Singapore . . . . .	1,582 „
Austria . . . . .	4,420 „

Total 634,608 lbs.

A considerable increase is shown in the sale of the fine Java citronella oil, the quality of which has so far remained the same, and which has a constantly increasing number of friends. Several large consumers who used to employ exclusively Ceylon oil, have gone over to the product from Java, and appear to find it worth while. For the better quality soaps only Java oil should be used, and the proportion be reduced by one half as compared with Ceylon oil.

Parry mentions in the "Chemist and Druggist"<sup>1)</sup>, in conformity with observations previously made by us, that pure citronella oils of commerce give different results with regard to their solubility in 80 per cent alcohol, some being quite soluble, whilst others, although quite soluble in 3 or 4 volumes, become slightly turbid on addition of 10 volumes of the alcohol. Parry found that, in general, the oils with low specific gravity give a perfectly clear solution, whilst those with a high specific gravity become turbid with 10 volumes of alcohol. He thinks that this is due to the greater preponderance of sesquiterpene in the high-gravity oils; he found that, when using alcohol of 81—83 per cent, the turbidity disappears almost, if not quite, whereas if the oils are adulterated with even very small quantities of petroleum, the turbidity remains the same even if 85 per cent alcohol is used.

**Clove Oil.** Although the local conditions of the production of this important article have been completely cleared up in the last few years through the information given in our Reports, there is still wanting a list of the shipments to the principal markets, which take place at regular intervals, such as exists for other colonial produce of less importance.

The Hamburg importers, who have their own branch establishments in Zanzibar, also preserve a haughty silence, and if the active commission agents in Holland did not now and then send some news, the only source of information would be the consular reports, which reach us always when the "news" they contain has become very ancient.

A statistical table from Holland gives the following figures:—

Stocks in Europe and New York on 1<sup>st</sup> August.

	1901	1900	1899
Holland . . . . .	64,500 bales	75,700 bales	80,300 bales
London . . . . .	18,300 „	22,300 „	36,800 „
Hamburg . . . . .	1,900 „	4,300 „	6,700 „
New York . . . . .	14,100 „	15,400 „	16,600 „
Totals	98,800 bales	117,700 bales	140,400 bales

Stocks in Europe and America on 1<sup>st</sup> January.

	1901	1900
Imports to 1 <sup>st</sup> August . . . . .	114,400 bales	116,600 bales
Deduct Stock on 1 <sup>st</sup> August . . . . .	20,300 „	39,300 „
Deliveries to 1 <sup>st</sup> August . . . . .	134,700 bales	155,900 bales
	98,800 „	117,700 „
	35,900 bales	38,200 bales

<sup>1)</sup> Vol. 59 (1901), 142.

A first glance shows already that these figures are intended to prove the favourable position of the article. Moreover, a rumour is spread about that the last harvest has given a smaller yield than had been expected.

It is, naturally, difficult to judge whether or not these reports have been influenced for certain purposes, so as to inaugurate an upward movement; but one glance at the stocks, which approach a whole year's harvest, will convince any careful observer that the possibility of a lasting improvement in the value is very doubtful. Up to the present the prices for forward delivery have undergone practically no change, for fluctuations of  $\frac{1}{8}$  or  $\frac{1}{4}$  cent are artificial, and have no importance for the real trade.

In Number 34 of the review "Export" we find, under the heading of economic notes from Zanzibar, an original article on the management of clove plantations, of which we give an abstract, in view of the great importance of this subject for all those who are interested in cloves or clove oil.

"An event has recently taken place in Zanzibar which is of the greatest importance for the islands Zanzibar and Pemba in the first place. This event is the opening of the business of a new English Company, which will chiefly be engaged in advancing money on loan. The Company was formed by Captain Hastings Neal, and will also be managed by him, with headquarters in Zanzibar.

The plantations in Zanzibar, among which clove plantations occupy the first place, have suffered, ever since the abolition of official slavery, from lack of labourers, i. e. unpaid labourers with whom the Arab proprietors were in the habit of working. For cash payment labour can still be had. In olden times the Arab had full power to deal with his slaves as he liked; the slave knew this, and fear made him work. Thursdays and Fridays belonged to him: on those days he looked after his small piece of land, and produced what he required for his personal wants. The remaining five days of the week belonged to his master, and it was then a question of either hard work, or severe punishment. Nowadays, in East Africa, in the countries which are under British authority, the slave has three days for himself, whilst he has to work four days for his master, which, however, he only does on extremely rare occasions. During a holiday which General Mathews spent last year in England, he succeeded in interesting financial people in the plantations, and in this way the Company mentioned above, under the management of Captain Neal, has been formed. The capital is £ 150,000.—. Captain Neal recently spent four months in Zanzibar, and made the necessary arrangements with the Government. The business was opened on the 1st August last. The Company intends in the first place to advance money, at a low rate of interest, not only on plantations, houses or land, but also on merchandise. By these means both the native proprietors of plantations and the foreign, mostly Indian, merchants would be enabled to extricate themselves from a state of affairs which has gradually become worse and worse until now it is unbearable.

The majority of the plantations in Zanzibar and Pemba are already mortgaged to Hindoos, and that mostly on terms which render the complete bankruptcy of the proprietor in nine cases out of ten only a question of time. An advance of a fixed sum at 15 per cent per annum may be called reasonable; much more frequently the business is done in this way, that an advance is made on the harvest against a mortgage on the plantation, a system which is also in force in Lamu, &c., for the produce of the fields. The price of cloves

fluctuated during the last harvest between 7 and 8 Rupees (15 Rupees = £ 1) per frazileh of 35 lbs. The harvest commences in August and lasts until the beginning of January at the latest. If now, for example, the proprietor of a plantation requires some money in March or April, the Indian merchant will not advance him more than 4 Rupees per frazileh. In this connection it should be mentioned that cloves are subject to a duty of 25 per cent on being brought into the town; this duty is of course paid by the Arab.

If there are on this plantation say 5000 trees, the crop under the most favourable circumstances would come to about 600 frazileh, the plantation having a value of about 7500 Rupees. The impecunious Arab of course declares that he expects a yield of 1000 to 1500 frazileh; the Hindoo knows that the plantation offers him sufficient security, and advances 4000 Rupees. With this money the Arab pays off old debts, makes some new purchases for his home and family, and discovers with alarm that he has scarcely enough left to cover the expenses of the harvest.

The gathering begins; the cloves are dried, and finally 100 frazileh are actually got together; 150 Rupees have been sufficient. The cloves are transported to the town; as he must sell rapidly to obtain cash he will not receive much more than 6 Rupees. 25 frazileh must be deducted for duty, and the net proceeds therefore come to  $75 \times 6 = 450$  Rupees.

If the Hindoo who advanced the money now suddenly appears on the scene, a bill is made up which makes the Arab's hair stand on end. The Arab is compelled to transfer his plantation and house to his creditor, and in a very short time he is a ruined man.

The object of the new English Company is to make an end to this state of affairs; it is, of course, to be expected, that within a short time a number of plantations will come into its possession, and for this reason it has made the necessary arrangements to undertake the management of plantations and carry on the trade in cloves and copra.

In order to start operations on a firm basis, the Company has leased the duty on cloves from the Government for a sum of £ 35,000.— per annum. This amount has been arrived at by multiplying the average harvest of the last ten years with the average price for the same period. The former was about 350,000 frazileh, the latter about 6 Rupees.

From these figures the number of clove trees in Zanzibar and Pemba may be estimated. If, namely, the average yield of one tree is taken as  $3\frac{1}{2}$  lbs., the result shows that the total number of clove trees in both islands comes to about  $3\frac{1}{2}$  millions; if the average value of each tree is about  $1\frac{1}{2}$  Rupees, the value of the clove plantations would amount to  $5\frac{1}{4}$  million Rupees, or rather more than £ 350,000.—. As the palm plantations, oil palms, mangoes and other fruit trees represent about an equal value, a quite respectable sum is arrived at. All this wealth would go to ruin if the Zanzibar Government had not taken the wise precaution of providing new blood in the form of capital. Without this, I reckon that in about 4 or 5 years' time nothing would have remained, at least of the very sensitive clove trees. As already mentioned, the plantations were in olden times, when slave labour still existed, broken up 3 or 4 times each year; now this is done on the best kept plantations at most twice yearly, whilst on many it is not done at all. What this leads to I saw shortly before my departure from Zanzibar, in May last. This happened at the plantation Kibodje, which the proprietor had mortgaged for 85,000 Rupees to a Hindoo; when the former died, the plantation became the latter's property and was let. The tenant naturally did nothing to the land; for two years the hoe had not been used. The strong palms could still stand this treatment, but not so the delicate clove trees; they were already half choked through the weeds, 4 or 5 per cent quite dead, 2—3 per cent as yet still alive, but in spite of their 25 or 30 feet height literally covered with creepers. The bulk of the trees looked feeble and miserable, and not a single one had formed fruit. According

to my estimate the whole harvest from these 25,000 trees would scarcely come to 100 lbs. of cloves.

What money and trouble may effect with such plantations can be seen in the Government plantation Dunga. This one had been practically abandoned by the proprietor, when it was taken over by the Government. At the present time the officials, especially Messrs. Lyne and Buzzacott, have so improved matters, that an average yield of 8 to 10 lbs. of cloves is expected from each tree, and that the value per tree may safely be estimated at 6 to 8 Rupees.

If in Zanzibar the plantations (cloves, cocos palms and fruit trees mixed) on a large scale, are managed judiciously and with sufficient capital, a return of 15 per cent on the capital may safely be expected, and it is in my opinion a sound basis to work upon, especially as a wealthy company can with some trouble and industry soon be brought to exert such an influence on the clove market, that it will more or less be able to fix the prices."

**Cochlearia Oil.** Contrary to previous observations<sup>1)</sup> that secondary butylamine, derived from the dextrogyre secondary butylthiocarbimide of oil of cochlearia, does not turn the plane of polarised light, Gadamer<sup>2)</sup> has recently detected a slight optical dextro rotation in secondary butylamine.

For secondary butylamine of a specific gravity of 0.7393, the values were:—

$$\alpha_D 15.5^\circ = +4.75^\circ \text{ (tube 100 mm. long)}$$

$$[\alpha]_D 15.5^\circ = +6.42^\circ.$$

As a proof that, in the reduction of secondary d-butylthiocarbimide into secondary d-butylamine, the asymmetric arrangement of the atoms had undergone no change, Gadamer re-converted the secondary d-butylamine into secondary butylthiocarbimide, and produced from the latter the d-butyl and d-dibutyl thio-urea, as well as the d-d-dibutylthiourea, all of which agreed in optical rotatory power, melting points, &c., with the ureas originally obtained from secondary d-butylthiocarbimide.

A 7.28 per cent aqueous solution of the hydrochloride of butylamine, showed at 20° and in a tube of 200 mm. a deviation:  $\alpha_D = -0^\circ 18'$ .

**Dacryodes Oil.** In our Report of October 1899, p. 28, we referred briefly to the essential oil of *Dacryodes hexandra* Grisebach, in connection with a paper by A. More. According to the author the oil contains l-sylvestrene; as, however, he had apparently only a limited quantity of material at his disposal, it seemed to us desirable to obtain confirmation of the presence of l-sylvestrene.

After several unsuccessful attempts we have recently succeeded in securing a small parcel of dacryodes resin, from which we have distilled the essential oil. The yield we obtained was a little over 16 per cent, which agrees fairly well with More. The oil is yellowish, mobile, and has a pleasant aromatic odour, reminding slightly of oil

<sup>1)</sup> Archiv d. Pharm. 237 (1899), 92.

<sup>2)</sup> Ibidem 239 (1901), 283.

of turpentine. Its specific gravity was found to be 0.8875 at 15°, its rotatory power  $\alpha_D - 13^\circ 20'$ . We are still engaged upon the investigation of the oil, and hope to communicate the results in our next Report.

**Elecampane Oil.** The essential oil of the root of *Inula Helenium* L., first examined by Dumas and Gerhardt, contains, as is well-known, a crystallising substance which had been designated as helenine. Subsequent work by Kallen showed that this substance is a mixture of two crystallising bodies, of which the bulk is a compound melting at 76°, which Bredt and Posth have recognised as lactone, and have called alanto-lactone. The body with the higher melting point (109—110°) which is found in small quantity along with alanto-lactone, had, according to Kallen, the formula  $(C_6H_8O)_x$ , and was named by him helenine.

J. Sprinz<sup>1)</sup> has undertaken the further examination of the last named body, which had so far remained practically unexamined. It was found that the compound, purified by repeated recrystallisation, melts at 115°, and shows a composition,  $C_{15}H_{20}O_2$ , similar in percentage proportion to that of alanto-lactone. In its chemical reactions the body behaves exactly like a lactone, and the author for this reason designates it as isoalanto-lactone. This lactone represents white prismatic crystals, which are soluble in benzene, ether, chloroform and absolute alcohol. It is recrystallised without change from hot soda solution; but by prolonged heating with soda solution, say for 5 or 6 hours, it is converted into the sodium salt of isoalantolic acid, which is precipitated when hydrochloric acid is added. When melted it is again converted, with liberation of water, into isoalanto-lactone.

Isoalantolic acid forms well-characterised salts and esters. The amide of the acid melts between 237 and 239°, and separates out, in the form of white fascicular crystals, when an alcoholic solution of isoalanto-lactone is saturated with ammonia. Isoalanto-lactone is converted into hydroisoalanto-lactone  $C_{15}H_{22}O_2$  by reduction with sodium amalgam and water. The melting point of this compound lies about 166°. When heated with soda solution it forms hydroisoalantolic acid melting at 123°. The amide of this acid, obtained like that of isoalantolic acid, melts at 176°.

Isoalanto-lactone has the property of adding during reduction one molecule of hydrogen, and it is equally able to form a monohydrochloride with hydrochloric acid, when it is treated in absolutely anhydrous ether with perfectly dry hydrochloric acid gas. The compound  $C_{15}H_{20}O_2 \cdot HCl$  thus obtained melts at 153°; when reduced with sodium amalgam it is converted into hydroisoalanto-lactone. In

<sup>1)</sup> Ueber das Isoalantolacton, ein Bestandtheil der Wurzel von *Inula Helenium*. Arch. d. Pharm. 239 (1901), 201.

alcoholic solution, however, isoalanto-lactone absorbs two molecules of hydrochloric acid, with formation of a compound which remains liquid, and which can also be reduced with sodium amalgam into hydroisoalanto-lactone. On the other hand, hydroisoalantolactone and isoalanto-lactone monohydrochloride, when treated with hydrochloric acid in alcoholic solution, can be converted into isoalanto-lactone dihydrochloride, which again, when boiled with alcohol, passes over into the monohydrochloride and finally into isoalanto-lactone. From these experiments it may be accepted that two double linkages are present in isoalanto-lactone.

Gerhardt had already observed that his helenine treated with nitric acid yielded a nitro product. Sprinz also obtained from isoalanto-lactone a nitro compound, which could be reduced into a diazotisable body. During distillation with zinc dust, the odour of naphthaline was observed.

According to the above, isoalanto-lactone appears to contain an aromatic nucleus. Experiments made to convert isoalanto-lactone into alanto-lactone, have, with the material available, led as yet to no result.

### Essential Oils, Messina and Calabrian.

Although the high prices of these essential oils, which had remained at the same level during the winter months, have, for several reasons, in the course of the summer months partly given way for lower quotations, there has been no noticeable increase in the demand from abroad. As a consequence, the export during the last few months, like that of the first months of the year, shows a decline as compared with the corresponding months of the previous year, as will be seen from the following table:—

	1901	1900
Exports in January . . .	76,642	97,294 kilos
"    February . . .	65,735	77,294 "
"    March . . .	61,323	69,635 "
"    April . . .	45,244	62,671 "
"    May . . .	53,396	48,595 "
"    June . . .	48,142	59,429 "
"    July . . .	35,395	46,034 "
Total, January to July	385,877	460,952 kilos.

**Bergamot Oil.** Owing to the small consumption and the absence of a more animated demand from abroad, the prices, which until March had remained at their highest level of about 21 to 23 Marks, have dropped gradually to about 16.50—18.50 Marks, but after a short time they have recently again risen to 18—20 Marks.

The quantity of this oil at present in stock does probably not exceed 5000 kilos; there is therefore little chance that the quotations will drop before the new oil comes in.

At the commencement of the summer the prospects of the new harvest were very promising. After the poor flowering period of the previous year, the trees now carried an exceptionally rich quantity of blossoms, which justified the highest expectations. But unfortunately the weather conditions later on were unfavourable, as the occasional showers, which in June and July interrupted the great heat, caused enormous quantities of the delicate fruit to fall off the trees. Although the hope of an exceptionally good harvest has thus disappeared, the expectations may yet be called satisfactory, and will probably result in a good medium crop.

It is believed that the ester-content will be found to be high, as the oil pressed from the fallen fruit showed a higher content than that pressed last year at about the same time.

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A pamphlet by Dr. Salvatore Gulli: *Il metodo della saponificazione nell'analisi della essenza di bergamotto* has been published as a special issue of the Report of the Chamber of Commerce of Reggio Calabria for the year 1900—1901. The principal matter contained in this pamphlet may thus be briefly summarised, that the saponification should not be taken as the only method of examination, nor the ester-content as the exclusive criterion by which the quality of a bergamot oil is to be judged. We have repeatedly expressed the same opinion, the last time in our Report of October 1900 p. 24; we may therefore be excused from again referring to this subject, particularly as the author several times quotes our remarks in the same sense.

But in another respect the pamphlet interests us greatly, namely in making us acquainted with a new adulterant, concerning which Gulli has recently also contributed an article to the "Chemist and Druggist"<sup>1)</sup>.

As, on the one hand, the addition of turpentine, and also of distilled (fractionated) bergamot oil, modifies the physical and chemical constants (specific gravity, optical activity and ester-content) of the pressed oil to such an extent that adulteration by these means is readily detected; and as, further, the value of bergamot oil is still often judged by the ester-content, attempts have been made to discover new adulterants, which would cause the smallest possible modification of the constants of the oils to which they are added. Such an adulterant, according to Gulli, is turpentine oil through

<sup>1)</sup> Vol. 59 p. 383.

which a current of hydrochloric acid gas<sup>1)</sup> has passed. By this treatment turpentine oil is said to acquire an acid number corresponding to about 18 or 20 per cent of linalyl acetate, whether the chloro-derivative thus obtained be pinene hydrochloride or dipentene dihydrochloride. According to Gulli, the turpentine oil so treated can be added to bergamot oil in the proportion of 5 to 10 per cent without much altering its constants; the greatest reduction of the ester-content thereby obtained comes to about 1 or 2 per cent.

The author examined three samples of commercial bergamot oil, which had the following constants:—

Specific gravity at 15°	0.882	0.8817	0.8810
Optical rotation . .	+ 10° 50'	+ 8°	+ 6°
Ester-content . . .	36.05 per cent	36.75 per cent	36.40 per cent.

All three samples were adulterated in the manner described, the first two containing almost 5 per cent and the third at least 10 per cent of turpentine oil treated with hydrochloric acid gas.

For this reason Gulli thinks it advisable to guard against this adulterant in future, and he recommends fractional distillation instead of saponification. But in his opinion the adulteration is best detected, if several grammes of the suspected bergamot oil are boiled with alcoholic potash solution in a platinum dish and the liquid evaporated, after which the residue is heated until all organic matter is removed; it is then treated with water and the filtered solution, acidified thoroughly with nitric acid, is tested with nitrate of silver.

As caustic potash is rarely quite free from potassium chloride, it is, of course, necessary to determine beforehand by a separate test whether it is suitable for the purpose. A better plan is to use for the saponification an alcoholic solution of sodium ethylate, which can be made by dissolving a little sodium in strong spirit of wine. But could not the same purpose, i. e. the detection of chloro-compounds, be effected in a much simpler manner, by testing the products of combustion of bergamot oil for hydrochloric acid, as is done with oil of bitter almonds?

Up to the present no oil has come into our possession which has been adulterated in the manner described by Gulli.

**Oil of Lemon.** The state of the market of this essential oil during the last five months has caused great surprise, as the prices, which at the time when our April Report was published were quoted at about 8.25 Marks, have gradually dropped to about 6.25 Marks.

<sup>1)</sup> Gulli mentions in his pamphlet that this can be done either by heating a mixture of manganese peroxide, common salt, and sulphuric acid, or more easily by heating commercial concentrated hydrochloric acid. This, however, could hardly be the same!

This peculiar symptom is due to three causes, of which two have already been mentioned in our April Report, when, however, their full effect could not yet be appreciated:—

1. The small demand from abroad for export fruit, and
2. The exceptionally high yield of essential oil of the lemons. We mentioned at the time, that the increase in the production through the high yield of essential oil was calculated at about 15 to 20 per cent; as a matter of fact, this estimate was subsequently found too low, as the fruit, as late as the end of March and until the middle of April, gave such a rich yield, as otherwise only occurs in the first few months of the manufacturing season.
3. The fact that the export of fruit in brine, which usually begins in March and then generally puts an end to the manufacture of oil, has this year been exceedingly limited, in consequence of which a large quantity of fruit became available for the manufacture of essences and lemon juice.

The quantity of essential oil manufactured for these three reasons during the spring months March and April, i. e. after the close of the season (15<sup>th</sup> March), is estimated at about 50,000 kilos. Such an important addition to the original estimate was bound to depress the prices, the more so as it coincided with an abundance of blossoms promising a good harvest for the following year. This accounts for the backward tendency which has continued since the end of March.

The present stock of old lemon oil may perhaps come to about 40,000 to 45,000 kilos, of which a large proportion is held by exporters; it is to be expected that this stock will be considerably lower by the time the new season's essence is placed on the market.

The prospects of the new season are on the whole favourable, as the crop from the lemon trees, like all other Sicilian products, will this time be a very good one. In many districts, especially on the North coast, complaints are made that the fruit has suffered much from insects (*pidocchi*).

The adulteration of oil of lemon with citrene is increasing every day, and makes existence still more difficult for the honest merchant than it was at the time of the turpentine-oil adulterations, against which some protection at least was possible.

Two new compounds have been discovered in oil of lemon by H. E. Burgess<sup>1</sup>). If 3 to 4 litres of the terpene mixture obtained in fractionating lemon oil, are shaken with a solution of sodium bisulphite, the separation of a crystalline double compound will be

<sup>1</sup>) Chemiker-Zeitung 25, 602; Chem. Centralblatt 1901, II, 419.

observed. After purification an aldehyde may be abstracted from this compound, which has an odour reminding of cocoa nut oil, boils at 80 to 85° under 15 mm pressure, and at 20° has an index of refraction  $n_D = 1.4314$ . This aldehyde yields an oxime of the melting point 35°, and on oxidation an oily acid. (It is probably a question of nonyl or decyl aldehyde.)

The second new body is obtained in the form of crystals, when lemon oil is dissolved in an equal volume of acetone, and, after adding one fifth volume of water, the aqueous acetone solution which separates out, is left standing for 24 hours. The crystals which separate at the surface of the solution are recrystallised from alcohol and ether; they then have a melting point of 145°, and, in alcoholic solution, show clearly a blue fluorescence. The compound yields a crystallising dibromide, and, on oxidation, oxalic and carbonic acids.

This is evidently the same body which Theulier<sup>1)</sup> has lately isolated from the residue remaining from the distillation of lemon oil, and which E. Schmidt<sup>2)</sup> has quite recently made the subject of an examination. By treating this residue with ether, and recrystallising the crystalline deposit thereby remaining undissolved, first from a mixture of acetone and methyl alcohol, and subsequently from dilute spirit of wine, the last-named investigator obtained the compound called by him citroptene (citriptene) in colourless needles or column-shaped crystals, which melted at 146—147°, and of which the elementary analysis gave values corresponding to the formula  $C_{11}H_{10}O_4$ . This would show that citroptene is identical with limettine, which Tilden and Beck separated from oil of limette, and for which they found the same composition and the same melting point. For the rest, citroptene, according to Schmidt, shows, like bergaptene from bergamot oil, the character of an acid anhydride, or lactone; it seems to belong to the group of dioxycoumarins, and to be an isomer of dimethylesculetine or dimethyldaphnetine derived from phloroglucinol.

Besides citroptene, Schmidt discovered in the residues of lemon oil, in addition to other compounds, a phenol melting at 89°, which dissolves in sulphuric acid with a dark red colour, but which does not react with ferric chloride.

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In our Report of April 1900 we have called attention to some shortcomings in the method for determining the citral in oil of lemon which has been proposed by J. Walther<sup>3)</sup>. Walther now feels it his duty to reply<sup>4)</sup>, and he endeavours, by means of numerous experiments, to prove the undoubted accuracy of his method.

1) See our Report April 1901, 30.

2) Apotheker-Zeitung 16 (1901), 619.

3) Pharm. Centralhalle N. F. XX (1899), 621.

4) Ibidem N. F. XXI (1900), 585.

Unfortunately we have had so far no time to continue our previous researches, but we will naturally not leave the question unanswered; on the contrary, we will undertake further experiments in order to be able to reply to Walther's recent arguments. We feel the necessity of this all the more, as we attach the utmost importance to the subject itself, and we would be only too pleased if the utility of Walther's method were confirmed, which, however, we cannot help doubting, in face of the experience we have up to now gained.

**Oil of Orange, sweet.** The remainder of last year's oil has nearly all been sold; there are now probably not more than 2000 kilos in the country, and these are also almost exclusively in the hands of exporters.

If, in spite of this, the prices of this essence have dropped in April to about 11.50 Marks, and since then have not gone higher than 12.25 Marks, this must be chiefly attributed to the favourable condition of the blossoms in the spring; these have on the whole developed satisfactorily, although in this case also the exaggerated hopes have not been fulfilled, and only a medium harvest is expected.

The present quotation of new sweet orange oil is low, and with a normal yield of oil it may probably remain at this level during the first months of the manufacturing season. Much lower prices can scarcely be expected, for the manufacture of oil (as we have already pointed out in previous Reports) would be unremunerative if the prices declined still further, and the growers would then find a better use for the fruit.

**Eucalyptus Oil.** For crude oil of the globulus species, the African product has now for some time made its influence felt, and that at prices, at which the Australian distillates of equal percentage cannot be supplied. A few Algerian distillers produce from 6000 to 10,000 kilos per season, and guarantee the eucalyptol-content precisely like their Australian competitors.

For the further manufacture of cosmetics the brownish crude oil, with its disagreeable odour, is not suited; for such purposes it has to undergo careful rectification. We therefore supply only the rectified oil, and we use our best endeavours to bring about the adoption, by the large consumers, of the pure crystallising eucalyptol in the place of the oil. Further particulars on this subject will be found at the end of this Report.

In describing a number of new species of eucalyptus, R. T. Baker<sup>1)</sup> mentions some new eucalyptus oils.

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<sup>1)</sup> On some new species of Eucalyptus. Proc. Linn. Soc. of N. S. Wales 1900. Part II, p. 303.

Oil of *Eucalyptus delegatensis* (White Ash, Silver-topped Mountain Ash). Yield 1.76 per cent. This oil has a pale lemon colour. It consists chiefly of 1-phellandrene, and contains neither cineol nor eudesmol. Specific gravity at  $15^{\circ} = 0.8602$ ;  $[\alpha]_D = -68.12^{\circ}$ .

Oil of *Eucalyptus intertexta* (Spotted Gum). The yield varies, as was proved by several trial distillations; the maximum does not exceed 0.64 per cent. The crude oil has a brownish yellow colour, and does not answer the requirements of a good quality oil. It contains no phellandrene, but, on the other hand, a large proportion of d-pinene. Specific gravity at  $15^{\circ} = 0.9078$ ;  $[\alpha]_D = +10.7^{\circ}$ . Cineol-content in the crude distillate about 37 per cent.

Oil of *Eucalyptus Morrisii* (Grey Mallee). Average yield 1.69 per cent. The oil, even after being rectified, has a faint colour, and possesses the odour of aldehydes. It consists mainly of d-pinene and cineol (more than 50—60 per cent), but contains neither phellandrene nor eudesmol; for these reasons it may be called a good oil. Specific gravity at  $15^{\circ} = 0.9097$ ;  $[\alpha]_D = +6.7^{\circ}$ .

Oil of *Eucalyptus viridis* (Green, Red, or Brown Mallee). Yield 1.06 per cent. The oil has a pale brownish yellow colour. Its odour reminds of cuminaldehyde. It contains less than 10 per cent of cineol, but neither phellandrene nor eudesmol. In the higher boiling fractions cuminaldehyde (?) was detected; in addition to this 1-pinene was found in this oil. Specific gravity at  $15^{\circ} = 0.9006$ ;  $[\alpha]_D = -8.90^{\circ}$ .

Oil of *Eucalyptus vitrea* (White Top Messmate). Yield 1.48 per cent. The crude oil is colourless, it contains much phellandrene, a little more than 20 per cent (up to 26 per cent) of cineol, and, in the higher boiling fractions, citral. Specific gravity at  $15^{\circ} = 0.886$ ;  $[\alpha]_D = -33.92^{\circ}$ .

In a short note<sup>1)</sup> on eucalyptus oils, Baker and Smith give the following figures for the oil of *Eucalyptus melliodora*: specific gravity of the crude oil 0.905, and of the rectified oil 0.902, the latter containing 58 per cent of cineol. They further state that the cineol-content of the oil increases towards the winter, but they are of opinion that the higher percentage of cineol has no influence on the specific gravity.

Parry<sup>2)</sup>, however, does not agree with this statement. In his opinion such a high percentage of cineol as that found by Baker and Smith is not consistent with the low specific gravity given by them. He examined an oil which was without doubt distilled from the leaves of *Eucalyptus melliodora*, and obtained figures which are

<sup>1)</sup> The Chemist and Druggist, vol. 57 (1900), 294.

<sup>2)</sup> Ibidem vol. 58 (1901), 588.

slightly different, viz: with a content of 52 per cent of cineol the specific gravity at  $15^{\circ} = 0.917$ , and the rotatory power  $\alpha_D = -0^{\circ}37'$ .

In our Report of April 1901, page 35, we mentioned that, according to H. G. Smith, the oil of *Eucalyptus macarthuri* contains principally geranyl acetate. We had an opportunity of examining a comparatively large sample of this oil which we had obtained through the courtesy of Mr. Smith; although the examination is not yet complete, we have been able to confirm Mr. Smith's results. The oil, which had a fairly dark colour and a very pleasant aroma, showed physical constants which were nearly the same as those already given, viz., specific gravity at  $15^{\circ} = 0.929$  and  $\alpha_D = +0^{\circ}48'$ . Saponification with alcoholic potash solution gave the number 182, which corresponds to 63.70 per cent of ester  $C_{10}H_{17}OCOCH_3$ . After acetylising, the saponification number rose to 243.7, which, calculated on the ester  $C_{10}H_{17}OCOCH_3$  gave a percentage of 85.2. The bulk of the alcoholic compounds consists no doubt of geraniol, which, as far as it is present in the esterified state, appears to be combined almost exclusively with acetic acid. But whether small quantities of other alcohols may not be present as well, is, as yet, an open question.

From the high-boiling fractions, after standing for some time, a crystallising body is separated out, which, according to Smith, is still somewhat mystic eudesmol. At this moment we have not yet completed the examination of this body.

According to H. G. Smith, (and as already mentioned in our April Report p. 34), the body which imparts to many oils of eucalyptus the odour of cuminaldehyde, and which had hitherto always been taken for cuminaldehyde, is probably not at all identical with the latter, but, on the contrary, quite a different compound.

Smith has recently proved<sup>1)</sup> by a detailed examination, that his supposition is correct; he calls the aldehyde aromadendral, following the notation *Aromadendrum* used by W. Anderson for the genus *Eucalyptus*. For its production Smith used the oil of *Eucalyptus hemiphloia*, from which, after removal of the portions boiling below  $195^{\circ}$ , the aldehyde was separated by extraction with bisulphite solution. The aldehyde was obtained from the well-pressed and washed double compound in the form of a mobile liquid of a faint yellow colour, having a not unpleasant odour, somewhat more aromatic than cuminaldehyde. The yield was about 3.3 per cent of the crude material; the specific gravity of the aldehyde, at  $15^{\circ}$ , 0.9478, and the optical rotation  $[\alpha]_D = -49.19^{\circ}$  at  $22^{\circ}$ . The boiling point lies at  $210^{\circ}$ , but it appears that decomposition already occurs at that temperature. The composition corresponds to the formula  $C_{10}H_{14}O$ . The oxime

<sup>1)</sup> Journ. and Proc. of the Royal Soc. of N. S. Wales, Vol. XXXIV (1900).

prepared from the aldehyde melts at  $84^{\circ}$ , the phenylhydrazone, under decomposition, at  $105^{\circ}$ ; with  $\beta$ -naphthylamine and pyruvic acid it is said to produce a naphtocinchonic acid melting at  $247^{\circ}$ . With chromic acid mixture only the aldehyde group is oxidised, whereby an acid  $C_{10}H_{14}O_2$  is formed, having the melting point  $110^{\circ}$ . If, however, the pure aldehyde is treated with alkaline solution of permanganate, a fairly energetic reaction occurs, a considerable amount of heat being evolved. One of the products of oxidation of this process is, in Smith's opinion, probably cineol (?); another is an acid of the melting point  $259-260^{\circ}$ , which, on being heated, is converted into its anhydride melting at  $152^{\circ}$ , and which, consequently, is not identical with cineolic acid.

Of a purely botanic interest is a work by the well-known botanists Deane and Maiden (already frequently quoted in our Reports), who communicate some observations on new species of eucalyptus of New South Wales<sup>1</sup>). They describe and illustrate as such the following:—

1. *Eucalyptus affinis*, a fairly large tree which attains a height of 80 and a diameter of a little more than 2 feet. It appears to be related to *E. sideroxylon* A. Cunn., and *E. hemiphloia* F. v. M.; others regard it as a bastard of *E. hemiphloia* var. *albens* and *E. sideroxylon*.
2. *Eucalyptus Cambagei* D. et M., a small or medium sized tree, which doubtless is closely related to *E. goniocalix*, but also shows a close connection with *E. Stuartiana*.

As a new variety the above botanists mention *Eucalyptus Stuartiana* F. v. M. var. *parviflora*, whose fruit is very similar both to that of a variety of *E. tereticornis* with small fruit, and to that of *E. Stuartiana*, but in other respects this variety more closely approaches the last-named species.

In conclusion the authors give some supplementary information concerning the species already described: *Eucalyptus eugenioides* Sieb., *E. pulverulenta* Sims., *E. punctata* D. C., *E. quadrangulata* D. et M., *E. squamosa* D. et M., *E. stricta* Sieb., as also a cross between *E. siderophloia* Benth. and *E. hemiphloia* F. v. M.

**Field-balm Oil.** For the essential oil prepared from the fresh leaves and flowers of *Melissa Calamintha* L., mentioned in our last Report, we have during the summer collected sufficient material, to distil about  $1\frac{1}{2}$  kilos at our Bodenbach works. Next year we hope to be able to produce it in larger quantities.

**Geranium Oil.** The position of these oils, which are indispensable to the perfumer, is throughout very favourable. The

<sup>1</sup>) Proc. Linn. Soc. of N. S. W. 1900, part I. p. 104.

price of African oil has advanced considerably, owing to the scarcity of other sorts, and the quantities produced are rapidly taken up by the consumers. The *Réveil agricole* of 26<sup>th</sup> May last, contains a long article on the cultivation of geraniums, in which it is strongly recommended to take up that industry energetically, as a price of 5 to 5.50 francs would readily be paid by the distillers for 100 kilos of the fresh plant. At this rate the gross revenue from a hectare (nearly 2½ acres), which produces 40,000 kilos, would be 2000 francs, and that for a plant for which the land is only required during five or six months. The author, Mr. Jules Grec, recommends the geranium growers to erect the necessary installations for the distillation, and to carry on that process themselves, thereby retaining the large profit which now goes into the pockets of the distillers. He admits, however, that the majority of the producers would not be able to bear the expense of laying down a distilling plant. Like all rapidly growing plants, geraniums require a good deal of manure, (especially that kind which quickly decomposes), and an equally large supply of water. The fields in the districts of Grasse, Le Loup and Cagnes at first yielded excellent results, but, owing to the manner of irrigation, they have become so exhausted, that the production diminishes considerably from year to year, in spite of the fact that the quantities of manure are doubled; and the cultivation of geraniums, like that of other aromatic plants, and especially peppermint, has thereby become almost impossible.

He prophesies that the fate of geranium will be precisely the same as that of violets, of which the cultivation has moved away entirely to Vence and neighbourhood. The geranium oil from Southern France differs so little from fine Algerian oil, that the decidedly higher price can hardly be justified, and is paid only by purchasers who specially prefer the former. The Spanish distillate which has a particularly fine aroma, undoubtedly occupies the first position with regard to quality. For the highest grade products, and especially for the tobacco industry, the last-named quality is indispensable, but the whole yield of it does not exceed a few hundred kilos, which are generally sold already before the distillation commences.

The situation in Réunion is unaltered. Since several years already the production is unable to meet the demand, and many consumers have been compelled to turn to the African oil, whereas the reverse used to be the case. Our buyer in St.-Denis (Réunion), a trusted correspondent of many years, who had an extraordinary knowledge of this trade, has, unfortunately, died, and we have not yet been able to find a substitute.

The state of affairs with regard to East-Indian geranium oil (so-called palmarosa oil) is very unpleasant. The production has not come up to the most modest expectations. Genuine first

quality, which answers the highest requirements, was only obtainable in very small quantity — a few pots — right at the commencement of the season; shortly afterwards only second grade oil could be bought, which, in spite of the greatest reluctance, had to be approved so as to avoid the risk of losing the chance altogether. As early as the beginning of January this year the buying season in Bombay had come to an end, and all the good oil was held firm; in March even secondary qualities were no longer to be had. The cause of the failure of the distillation is to be found in the exceptional drought, which prevailed in Kandesh during the harvest time, and which has decimated the plants.

It will readily be understood that such a crisis greatly favours adulteration. In the first place, the fine oil from the young herb is mixed already in India with the less valuable oil from the more mature herb, as the latter by itself is difficult to sell. Such a mixture represented this year's "first quality" oils. A second baptism is next practised either at Bombay, or else in Europe, especially with fractions of citronella oil. The analyses, published in our April Report, showed that of nine samples of oil examined, only three could be classified among the normal oils. If the market were sounded at the present time, the result would be much more unfavourable still.

Some slight consolation is, however, to be found in the latest reports from India, which say that the monsoon has this year for once burst early again (on the 10<sup>th</sup> June), and that consequently there is some hope of a good and opportune season for geranium oil.

With regard to the common so-called gingergrass oil, the situation is, if possible, still worse. The bulk of the supplies can hardly be recognised as such.

Jeancard and Satie<sup>1)</sup> have determined, by a long series of examinations, the chemical and physical constants of the geranium oil produced at Cannes. The figures, given in tabular form, present a review of the observations made during the whole course of the distilling season.

**Ginger Oil.** H. v. Soden and W. Rojahn<sup>2)</sup> some time ago discovered in ginger oil a sesquiterpene which had the, for this class of bodies, exceptionally low specific gravity of 0.872; as it could not be identified with any of the known hydrocarbons  $C_{15}H_{24}$ , they gave it the name of zingiberene. The statements made by these authors have recently been confirmed by O. Schreiner and Edw. Kremers<sup>3)</sup>. The latter isolated the sesquiterpene from the oil by fractional distillation under reduced pressure; they determined the boiling point of the

<sup>1)</sup> Sur l'essence de géranium de Cannes. Bull. Soc. chim. III. 25 (1901), 516.

<sup>2)</sup> Pharm. Zeitung 45 (1900), 414.

<sup>3)</sup> Pharm. Archives 4 (1901), 63.

hydrocarbon under 32 mm. pressure at 160 to 161°, and found the specific gravity 0.8731, at 20°, the rotatory power  $[\alpha]_D = -73.38^\circ$ , and the index of refraction  $n_D = 1.49399$ . They also prepared various derivatives of zingiberene, such as the hydrochloride (melting point 168°), the nitrosite (melting point 97°), the nitrosate (melting point 86—88°) and the nitrosochloride (melting point 97°).

**Jasmine "Schimmel & Co."** The constantly expanding consumption affords the best proof of the increasing advantage which the perfumery industry derives from this product. Although the sanguine expectations, that it would be possible to supplant the natural with the artificial product, have not been quite realised, the fact cannot be gainsaid, that in case of a bad harvest of flowers the perfumer has a valuable reserve in the artificial oil. From this point of view, even the opponent of the chemical tendency in the perfumery industry must feel a certain amount of sympathy for these new inventions and creations of diligent research.

E. Erdmann<sup>1</sup>), in a "Note on oil of jasmine flowers", states, contrary to A. Hesse's work, that he has been the first to communicate the presence of benzyl acetate, benzyl alcohol, linalool, and methyl anthranilate in oil of jasmine flowers. He also claims to have detected methyl anthranilate in the oil obtained by extraction, whilst A. Hesse could only discover this constituent in the oil obtained by the enfleurage method. For this reason he considers Hesse's opinion, that methyl anthranilate is only formed during the process of enfleurage, as incorrect. On the strength of experiments made at Grasse with jasmine flowers, Hesse had also expressed the opinion that a considerable quantity of essential oil of jasmine (about nine times as much as the original content) was developed in the picked flowers during the enfleurage period. E. Erdmann considers that these experiments do not prove the case, and that the generation of aromatic substances in the picked flowers is out of the question. He also appears to disagree with our suggestion, that possibly oil-constituents might develop in the rose flowers after gathering. The experiments to solve this problem which we have already made and are still continuing have not yet been concluded. But as E. Erdmann himself has as yet made no experiments whatever on this subject, his objections do not carry any weight. The processes which bring about the development of aromatic substances in the organism of the plant are as yet so little known, that it would be risky to reject a new theory thereof *a priori* as incorrect.

We avail ourselves of this opportunity to point out, that the principal constituents of oil of jasmine flowers have first been discovered (in the year 1895) in our laboratories, a fact which can be proved

<sup>1</sup>) Berliner Berichte 34 (1901), 2281.

at any time by the paper deposited on 27<sup>th</sup> December 1895 with a public notary of this town<sup>1</sup>). The artificial oil of jasmine subsequently placed by us on the market in April 1896, contained, in addition to other substances discovered by us in oil of jasmine, not only synthetic benzyl acetate and benzyl alcohol, but also synthetic methyl anthranilate. It follows that we were the first to employ these three bodies in the production of artificial oil of jasmine, and to designate the product publicly as such. Since our artificial oil of jasmine was at everybody's disposal as an inexpensive, readily available material for examination, the task of detecting these principal constituents also in the natural oil was rendered much easier to other investigators. Not until our synthetic oil appeared on the market has oil of jasmine been the subject of more general interest.

**Juniper-berry Oil.** Fine distillates from berries had become so scarce at the approach of the new harvest, that several orders had to remain unexecuted. The first consignments of new Italian berries have meanwhile been worked up, and the deficiencies made good.

The result of this year's harvest, both in Italy and in Hungary, is only middling, but the demand is so great, that buyers should be prepared for higher prices of fine berry oil.

Juniper-berry oil can be produced at any price, by mixing it with Hungarian oil, which is obtained as a by-product in the preparation of juniper brandy. The last-named oil, however, is not normal, as the valuable parts containing the actual aroma of the berries, have passed over into the brandy and are absent from the oil. A pure distillate from berries can only then be supplied advantageously, when the distillation is carried on along with the preparation of the juice of juniper berries.

**Lavender Oil.** The reports on this important article, received from the leading districts, are on the whole favourable.

**Alpes-Maritimes and Basses-Alpes.** In both these departments the harvests are a good average, and large quantities of high-grade essences will thence be placed on the market. These essences are produced in the above departments with a linalyl acetate content up to 42 per cent, whilst essences of less than 30 per cent are seldom met with. We are informed that of the 1900 product fairly large stocks are still in hand. Low prices are expected.

**Drôme and Vaucluse.** Heavy showers in the spring have had a very beneficial effect on the growth of the plants, and even in the summer the latter have not suffered from drought; they looked extremely well, and many landed proprietors have therefore taken up the distillation. On the other hand, complaints

<sup>1</sup>) Report April 1896, p. 60.

are heard that in spite of the favourable state of the weather, the yield of oil is not good. The average is estimated at approximately the same as last year. Owing to fairly large stocks of oil from previous seasons, low prices may probably be expected.

**Gard and Hérault.** In these departments the great drought has had an injurious effect on the development of the plants, and on the yield of oil in the distillation. The result must be called "medium".

The sum-total of the impressions made by the foregoing is, that a continuance during this season of the very low prices which have ruled up to now, may be looked for, or that the quotations may perhaps even go a little lower still.

In our Report of October 1900 we mentioned on page 41 a fresh attempt, on the part of a firm at Grasse, to deceive us with an adulterated lavender oil. The ester-content had been raised by the addition of resin, and it was expected that this would not be detected, and that an opportunity would thus be given to take revenge for the steps previously taken by us, by which several firms had been greatly inconvenienced. Some time ago we learnt that the oil in question originated from the same firm who had on a former occasion attempted to raise the ester-content by adding ethyl succinate; but recently the firm who had supplied the oil adulterated with resin wrote to us, that they had been the victims of an unscrupulous "colleague", who had laid a trap for them. They earnestly beg our pardon for the regrettable incident, and ask us to favour them again with our confidence.

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The German Pharmacopœia requires that lavender oil should make a clear solution with three parts of dilute alcohol (68 to 69 per cent by volume). In consequence of complaints which have reached us from various quarters, that the oil received did not answer the requirements as to solubility specified by the Pharmacopœia, we have tested a series of good quality lavender oils with regard to their solubility in the dilute alcohol of the Pharmacopœia. The results are as follows:—

A lavender oil which has the ester-content required by the Pharmacopœia (29 to 30 per cent) makes a clear solution with 3 to  $3\frac{1}{2}$  volumes of 68 per cent alcohol, and with 3 volumes of 69 per cent alcohol. But the first-named solution with a large excess of alcohol shows immediately an opalescence, whereas the solution in 69 per cent alcohol at first remains clear when more solvent is added.

This, however, does not happen with lavender oils having a higher ester-content (about 40 per cent). In this case  $3\frac{1}{2}$  to 4 volumes of 68 per cent, and 3 to  $3\frac{1}{2}$  volumes of 69 per cent alcohol

are required to make clear solutions. The solution in 68 per cent alcohol very soon acquires a fairly strong opalescence, and retains this, even when more alcohol is added. The solution in 69 per cent alcohol remains clear, but in this case opalescence appears immediately upon adding more alcohol, contrary to what happens with lavender oils less rich in ester.

It is therefore quite possible that the lavender oil (according to the strength of the dilute alcohol and the ester-content of the oil itself) may not answer the requirements of the Pharmacopœia; in fact, this will always be the case, if the test is made with dilute alcohol which has the lowest alcohol-content allowed by the Pharmacopœia. Such occurrences would not be possible, if the Pharmacopœia specified a dilute alcohol of quite definite strength, as, for example, 70 per cent by volume. With  $2\frac{1}{2}$  to 3 volumes of such alcohol all lavender oils make clear solutions<sup>1</sup>).

We are at this moment still engaged upon the solution of the question, whether the varying solubility of lavender oils is only due to the ester-content, or perhaps, to a greater content of sesquiterpenes in the oils rich in ester. We will return to this matter in our next Report.

**Linaloe Oil.** The consumption of this oil is still growing; a large proportion is used for the production of linalool. The price has moved upward, and is at present firm, with somewhat reduced stocks.

The shipments from Mexico amounted in 1899—1900 to 16,424 kilos, value \$ 25,194.

**Oil of Mandarins, artificial, "Schimmel & Co."** As already mentioned in our Report of October 1900, our chemists have succeeded in discovering the body which imparts the characteristic odour to oil of mandarins, and in preparing this body synthetically. This is the methyl ester of methyl anthranilic acid, the preparation and use of which have been protected by two German patents Nos 122,568 and 125,308 granted to us. The bulk of oil of mandarin consists, as is well-known, of d-limonene; in addition to this the oil contains small quantities of dipentene, decylaldehyde, nonylaldehyde, linalool and terpeneol. Since sufficient data for the manufacture of an artificial oil of mandarins are available, we have taken it up with very satisfactory result. The artificial oil can scarcely be distinguished by the odour from the natural product, and the physical constants are also practically the same.

Commercial oil of mandarins has up to now only been an unimportant article of consumption, because the price is high, and the genuine oil could only be obtained with difficulty, and in small quantities. We believe, however, that there is a favourable prospect

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<sup>1</sup>) Compare also the remarks in this Report on the solubility of East Indian sandalwood oil.

for the artificial oil, which we are in a position to supply at half the price of the natural product, and we venture to hope that it will be well received. Samples are at the disposal of our clients.

**Neroli "Schimmel & Co."** There has been an exceptionally brisk demand for our original product, owing to the small yield of the orange flower harvest in the South of France, and to the high prices consequently obtained for the natural distillate. During the last few years the opinion has slowly but surely gained ground in wide circles, that this product of our invention must be reckoned among the best that science and practice have produced in this field. We are convinced that the price of genuine neroli oil would be much higher this year, if it were not kept down solely by our artificial product. Perfumers have therefore every reason for a sympathetic feeling towards the latter, even if they should not yet be users of it.

**Neroli or Orange flower Oil (French).** It is sufficiently well-known that, in consequence of animated speculation, the prices of orange flowers in the South of France have been driven up from 75 to 90 centimes, which led to an increase in the price of good quality oil to 425—450 fr. The yield at the commencement of the gathering season was on the average 1 kilo and 152 grammes per 1000 kilos flowers, but in the further course of the distillation it rose to 1 kilo 400 grammes and up to  $1\frac{1}{2}$  kilos. This fact, added to the presence of a comparatively large stock of the previous year's distillate, prevented a further increase in the prices, and caused a certain holding back, which has become latent in the form of a general flatness, and which may possibly bring about some slight further depression in the quotations. Favourable forward purchases before the beginning of the harvest enable us to compete successfully.

Eug. Theulier<sup>1)</sup> publishes a table in which the physical and chemical constants of a large number of oils of orange flowers from different sources have been marshalled together. The oils have all been produced this summer in the manner usually adopted in the South of France, i. e. by distilling the flowers with steam, without cohobation; they show some differences with regard to their quantitative composition and physical constants. The specific gravity fluctuated at 15° between 0.869 and 0.8726, the average being 0.8709. The optical rotation, at 23°, was found between  $+2^{\circ}50'$  and  $+7^{\circ}20'$ , with an average of  $+4^{\circ}48'$ . The linalyl acetate content rose from 8.08 to 14.70 per cent, and was on the average 11.27 per cent. But the percentage of methyl anthranilate appears to be particularly subject to fluctuations; it was found to be from 0.42 upwards to 1.10, equal to 0.70 per cent as the average of the 33 samples examined.

<sup>1)</sup> Caractéristiques des essences de fleurs d'oranger de la récolte 1901. Bull. Soc. chim. III. 25 (1901), 762.

For the determination of this ester, the method described by Hesse and Zeitschel was adopted.

Although the flowering season of the oranges commenced very late this year, owing to the long continuance of cold weather along the whole South coast of France, the yield of oil was comparatively high, thanks to the dry and warm weather which prevailed during the harvest. The yield fluctuated between 0.91 and 1.33 per cent; the flowers from Golfe-Juan and Vallauris gave the highest yield, whilst flowers with a smaller oil-content were produced in Biot, Le Bar, La Colle, Tourettes and other places. It was also found that rainy weather during the harvesting season had an unfavourable effect, for on rainy days the yield was smallest, and was then considerably below the average<sup>1</sup>).

Similar tests have been made by Mr. Jean Gras at Cannes, during this year's harvest of orange flowers and he has written to us on the subject as follows:—

"I have noticed that the optical rotation of neroli oil is higher this year than previously; in 1899 it fluctuated between  $+3^{\circ}22'$  and  $+5^{\circ}24'$ , in 1900 between  $+2^{\circ}$  and  $+5^{\circ}40'$ , and this year between  $+4^{\circ}20'$  and  $+7^{\circ}$ . I believe that this must be attributed to the drought which has prevailed during the whole harvesting season. The average yield has also been higher, as will be seen from the following table, which gives the constants of neroli oil of this year's yield from 23<sup>d</sup> May to 4<sup>th</sup> June. The observations have all been made with distilled neroli.

	Spec. grav. at 15 <sup>0</sup>	Opt. rot. at 22 <sup>0</sup>	Sapon. No.	Solubility in 75 p. c. alcohol at 24 <sup>0</sup>	Yield of oil per 1000 kilos
23 <sup>d</sup> May	0.875	$+5^{\circ}2'$	39	in two volumes	0.900
24 <sup>th</sup> "	0.874	$+4^{\circ}28'$	40	" " "	0.870
25 <sup>th</sup> "	0.875	$+5^{\circ}25'$	41	" " "	0.980
26 <sup>th</sup> "	0.875	$+5^{\circ}10'$	37	" " "	1.020
27 <sup>th</sup> "	0.875	$+5^{\circ}45'$	34	" " "	1.150
28 <sup>th</sup> "	0.875	$+5^{\circ}46'$	37	" " "	1.160
29 <sup>th</sup> "	0.874	$+6^{\circ}15'$	31	" " "	1.200
30 <sup>th</sup> "	0.874	$+4^{\circ}55'$	33	" " "	1.120
31 <sup>st</sup> "	0.875	$+5^{\circ}$	34	" " "	1.150
1 <sup>st</sup> June	0.874	$+6^{\circ}$	32	" " "	1.020
2 <sup>nd</sup> "	0.873	$+4^{\circ}40'$	36	" " "	1.210
3 <sup>d</sup> "	0.875	$+7^{\circ}$	39	" " "	1.400
4 <sup>th</sup> "	0.876	$+6^{\circ}46'$	34	" " "	1.500

In order to satisfy myself that my constants agreed with samples of neroli oil from other firms, I have obtained samples from various sources, and have found on the average an optical rotation of  $+5^{\circ}10'$  to  $5^{\circ}50'$ ."

**Orris Oil.** Since the publication of our last Report, the situation has gradually become still worse for the growers of the root in the neighbourhood of Florence.

<sup>1</sup>) Compare: Jeancard et Satie, "Sur les essences de néroli et de petit-grain". Bull. Soc. chim. III. 23 (1900), 605, and Report October 1900, 48.

In August we received the following information:—

“Owing to the continued decline in the prices, the purchasers abroad have so far bought as a rule only for their immediate requirements, but this could not prevent a gradual dwindling away of the stocks during the season, as the consumption of the article at the cheap quotations appears to have increased, and moreover little had been bought during the previous year. There are still about 200,000 kilos in hand from the last harvest, and the bulk of this may find purchasers before the new crop comes in, as there is a continued demand.

The holders of stock refuse as long as they can to accept the prices now obtainable, and only slowly small parcels are sold here and there, whose owners are either tired of waiting, or in want of cash.

The cost of production of Florentine orris roots, according to the conditions of the soil and the weather, comes, for the large producers, to a minimum per 100 kilos of:—

70 to 75 Lire for 2 years' cultivation,  
65 to 70   ”   ” 3   ”   ”   ”

the average price of slips being taken at 2 Lire per 1000 (during last year the average price was 4 Lire). This price of 2 Lire is taken so low, that with a still lower quotation the work would no longer pay.

100,000 slips yield in 3 years' time about 1400 kilos trimmed roots, and in 2 years about 950 kilos.

If grown on a small scale the article can no doubt be produced at less cost, for in such case the grower is at the same time labourer, who, along with other agricultural work, also personally attends to the cultivation of the orris root. But where the roots are cultivated on a large scale, where the proprietor, in accordance with the Tuscan custom, has to divide the harvest with the labourer in this manner, that the latter receives two-thirds of the production of orris root for his work, and is moreover paid one-third of the cost of trimming, which comes to about 18 Lire per 100 kilos of trimmed roots, the minimum cost of production is as stated above.

Here in Tuscany the proprietor lets his land to the tenant farmers, and receives from the latter, in lieu of rent, one third of the orris root produced; but he has to pay back to the tenant 6 Lire per 100 kilos = one third of the cost of trimming. Other expenses, such as discount, brokerage, and carriage, amount to 4 Lire per 100 kilos of trimmed roots. A hectare of land yields in 2 years about 1400 kilos of trimmed roots and in 3 years about 2000 kilos; on this basis, at a selling price of 60 Lire, the landlord would receive per hectare 196 Lire for two years' rent, and 280 Lire for 3 years, or say 98 and 93.33 Lire per hectare per annum, which, if compared with other products, is much too little.

The production on a large scale, under the present circumstances, is bound to decline, whilst the small growers are not able to produce a large crop, and at the utmost could not produce more than about one-fifth or one-fourth of a regular harvest. It follows that the crops will become smaller, a fact which in future must necessarily react on the quotations.”

In the meantime the new crop, which is much smaller in quantity than that of the previous year, has arrived on the market, and has met with a very brisk demand, in consequence of which the prices have advanced 4 to 5 Lire per 100 kilos. It is, however, believed that this increase is only due to the fact that the merchants wished to secure some of the new crop, and that it will not go any further. On the other hand, a return to the low quotations of the early part of August is considered out of the question, and, according to the reports from the principal firms, who are engaged in this

trade as a speciality (which reports all agree on that point), the prices for this season will at least remain at their present level.

We have made contracts for large quantities and have bought at an average price which has enabled us to reduce our quotations of orris oil yet a little further. We now carry on the manufacture of this important oil with quite new and peculiarly constructed apparatus, and thereby produce an article of the highest degree of perfection.

The liquid orris oil "Schimmel & Co.", in eight-fold concentration, introduced in April last, has been a complete success, and has been the subject of the most flattering appreciation by the highest experts. This product may have a great future as a serious competitor of ionone, which it excels in various respects. If it is taken into consideration that the cost of a 25 per cent solution of liquid orris oil is not higher than that of a 10 per cent solution of ionone, and if the two solutions are compared, the sympathy for ionone will cool down enormously. Our orris oil, with its persistent character, is used with excellent results for soaps, for which ionone, as is well known, is not suitable. A solution of the former retains throughout the same odour, but an ionone solution has now a violet-like odour, then a peculiar odour like cedarwood; hence the frequent complaints with which one has constantly to contend.

We strongly recommend trials in this direction, the results of which will be found to confirm what we have stated. It is our constant aim to improve the quality of our product to the highest possible perfection, and also to promote the large consumption by the perfumery industry, by reducing the price to the lowest level.

**Patchouli Oil.** It would seem that a reaction has set in with regard to this important perfume. In Penang double the old price is now asked for normal leaves, and lower offers are refused, so that no option is left but to submit to the higher demands.

The stocks in Europe, in so far as they have not been cleared altogether, consist of very inferior stuff mixed largely with earthy matter.

**Pepper Oil.** The high-boiling fractions of oil from black pepper have not again been examined since Eberhardt in 1887 occupied himself with this oil. From the fact that he obtained fractions having boiling points of 190 to 250°, and 250 to 310°, it was concluded that oil of pepper contains a sesquiterpene. This has recently been confirmed by O. Schreiner and Edw. Kremers<sup>1)</sup>, who have also succeeded in identifying the hydrocarbon with caryophyllene (whose physical constants were very similar), by preparing the nitrosite melting at 43°.

<sup>1)</sup> Pharm. Archives 4 (1901), 61.

**Peppermint Oil, American.** Since the publication of our last Report an enormous change has come over this important article, owing to the unfavourable conditions of the production. In Wayne County, State of New York, the yield of this year's harvest will scarcely come to one-half of that of the previous year. In many territories where the cultivation of peppermint used to be carried on, it has now entirely been given up.

In Michigan the situation is not much better. We reproduce here the original reports from a number of growers:—

**Nottawa, St. Joseph Co.** The low prices in February, March and April 1900 have put a complete check to the planting out of roots, so that in the spring no roots were available for transplanting. If everything which is now growing is planted out, there could be no production on a large scale until 1903.

**Menden, St. Joseph Co.** The cultivation in this section has not increased. Most of the stills are idle, and will not be started again until higher prices are obtainable for the oil. The wet weather will probably result in a small harvest.

**Casnovia, Muskegon Co.** Here about 100 acres of new plants have been bedded out, and about the same area of old plants. The production of oil will come to 4000—5000 lbs., against 10,000 lbs. in the previous year and 60,000 lbs. five years ago. The low prices have gradually turned the farmers from the cultivation of peppermint.

**Decatur, van Buren Co.** A large number of farmers have given up the cultivation of peppermint. The crop of herb will be at the most two-thirds of that of last year, and if the yield is not large, the falling off, as compared with 1900, will be very high. Everybody expects higher prices.

**Coldwater, Branch Co.** Taking all in all there are in this district scarcely 100 acres planted with peppermint. Many farmers in the neighbourhood have given it up entirely.

**Dowagiac, Cass Co.** In view of the low prices the production of peppermint oil has been completely given up here. Good land and good stills are available, but at the present prices nobody can make a living out of it.

**Almont, Lapeer Co.** A large number of farms have given up the trade. The harvest will not produce more than one-half of that of last year.

**Lawton, van Buren Co.** The plants bedded out in the spring are very few, and the crop will be very small, in consequence of the dry weather.

**Kalamazoo, Allegan Co.** One of the most important and reliable growers of peppermint reports, that in his district very

few new plants have been bedded out. Although a few fields of old plants appear to do well, the general average crop will be small. The new plants bedded out do not number one-half of those of previous years. The old fields look poorly. A large portion has been destroyed by frost. Although many reports are spread about for dishonest purposes, there can be no doubt that the production of oil in Northern Indiana, and in the South Western part of Michigan, will be considerably lower than before.

**Parkville, St. Joseph Co.** In our district the crop of this year is estimated at about 10,000 lbs. The estimates vary from one-half up to three-fourths of last year's yield. There is a firm expectation that in a few months the price will be \$ 2, and at the present time \$ 1.50 is already asked, a price which, however, has not yet been paid this season for crude oil.

**Mishawaka, St. Joseph Co.** The harvest will be smaller than for many years, and will hardly come to one-half of that of previous years. Many fields look so bad that it does not pay to cut the herb.

**Goshen, Elkhart Co., Indiana.** The peppermint industry has been given up, with the exception of some very small areas, and the apparatus have been pulled down, as general discouragement prevails on account of the low prices. The few remaining fields suffer from want of rain.

**Moorland, Muskegon Co.** The acreage is about the same as last year. One-half of the stills have not worked in 1900, and this year even fewer will be in operation.

**Decatur, van Buren Co.** Only one-half of an ordinary harvest is expected. Scarcely any new plants have been bedded out.

The foregoing reports are well adapted to create in Europe also a favourable opinion about this article. In the United States the prices during the last twelve months have slowly but constantly risen, from 80 cents up to \$ 1.25, i. e. fully 50 per cent. It remains an open question whether the hopes of the producers, to see this year prices of \$ 2.—, will be realised; but in view of the present state of affairs we do not consider this impossible. The quantity in stock at first and second hand has a considerable bearing on the course of the prices. As the following statistics show, the export has fallen off very considerably:—

#### Export of peppermint oil.

Fiscal year 1892 .	54,987 lbs.	Fiscal year 1897 .	162,492 lbs.
" " 1893 .	99,629 "	" " 1898 .	145,375 "
" " 1894 .	80,225 "	" " 1899 .	117,462 "
" " 1895 .	87,633 "	" " 1900 .	89,558 "
" " 1896 .	85,290 "	" " 1901 .	60,166 "

From this it might be inferred that the stocks are more important than is generally believed, and that they might, at a given moment, put a check upon a too rapid upward movement.

On the European continent transactions in American peppermint oil were very animated during the last few months, and many consumers have covered their requirements for the near future. In England also there was a brisk demand with the approach of the distilling season.

Our New York branch, which ranks among the leading buyers in America, deals only in the better qualities, of which the pick is used for our brand "F. S. & Co." which has now been in existence for 30 years. This brand represents the purest and best American oil obtainable.

**Peppermint Oil, English.** The reports from the English peppermint districts are one and all unfavourable. In consequence of the great drought the crop of herb has been small, but the quality of this year's oil is very fine, as usually in hot summers; and the plants are rich in oil.

The leading distillers ask prices which are about 15 per cent higher than last year. The common commercial qualities can, as heretofore, be bought at any price. Our quotations are still very low, as we had contracted for large parcels of 1900 distillate.

**Peppermint Oil, Japanese.** The tendency in Japan is firmer now than it was at the time of our last Report. This change is due to a large deficiency in the harvest in the province Yonezawa. The total result of this harvest was only 40,000 catties, against 70,000 to 80,000 catties in the previous year, and the situation would be very critical, if the crop in the province Bingo Bitchin had not been larger than that of last year, viz., 50,000 catties, against 30,000 in 1900.

Export of peppermint oil from Yokohama and Kobe  
from 1<sup>st</sup> January to 31<sup>st</sup> July 1901.

To Hong Kong . . . . .	14,551 catties
„ Havre . . . . .	1,975 „
„ India (Bombay, Singapore, &c.) . . . . .	1,113 „
„ London . . . . .	967 „
Total	<u>18,606 catties,</u>
or about 24,700 lbs.	

The foregoing figures may be taken to justify the favourable opinion which prevails for this article.

**Petitgrain Oil.** It is reported that the distillers in Paraguay have formed a ring, so as to keep the price of this article on a level proportionate to the cost of production. For this reason the quotations

have recently been higher. Through old contracts we are in a position to supply at substantially lower prices, and we would draw special attention to our reduced quotations.

**Rose Oil, Turkish.** We have received from a reliable source the following original report on this year's rose harvest:—

"The trees have come through the winter exceedingly well, and hopes were entertained for an abundance of flowers, until, just before the commencement of the distilling season, a good proportion of the fields suffered greatly, partly through drought, partly through hailstorms, frost and blight. In certain districts, at the foot of the Sredna Gora, the distillation has taken place under exceedingly favourable conditions, and it exceeds in quantity that of the previous year. In the deeper-lying valleys, however, the drought from the beginning to the end was so severe, that a large portion of the buds fell off the trees. In other districts also, and especially in those at the foot of the Balkans, not a drop of rain fell during the rose distillation, whilst large numbers of flowers were destroyed by hailstorms and blight. The old rose-trees have everywhere suffered exceedingly, and the idea which largely prevails, that such trees yield paying results for 30 years, has now been thoroughly disproved. The productiveness does probably not exceed eight to ten years.

The total quantity of rose oil produced this year is estimated at 3050 kilos. This amount is distinctly lower than that of last year, and is about at the level of previous normal years. The quality, however, is considered very high, both with regard to the odour and to the freezing point, and this is supposed to be due to more careful distillation, which was rendered possible by the comparatively smaller quantity of flowers. Of 100 samples which had been collected during a journey through the most varied districts, 80 showed a congealing point of 16 to 18° R., others 15° R., and only two samples 14° R.

On the whole, the total yield may be considered equal to that of a good average harvest.

With regard to the stocks of old rose oil, in view of the low prices large quantities have been bought on speculation. One firm, for example, supported by English capitalists, has made a regular raid on rose oil, without being very particular as to quality. The stocks still in its hands are estimated at 450 kilos; other speculators may possibly hold about 150 kilos, and small producers about 120 kilos, so that the total stock of last year's oil in Bulgaria may come to about 720 kilos.

As to the price, the new oil is estimated on the average at 560 to 600 Marks. If interest on capital is allowed for, the speculators would therefore appear to have made no particularly favourable bargain, and it is feared that they will endeavour to force the prices up; the alarming rumours already circulated, that the result of the harvest is a very small one, would seem to point to this. In order to keep the small producers from selling, the report has been spread about that the price would go up to Fr. 1000.

The figures published by the Statistical Office of Bulgaria show, that in 1900, 5846 kilos of rose oil have been exported. From 1st April 1900 to 1st April 1901 the export came to 5167 kilos.

These figures prove beyond a shadow of doubt that adulteration still flourishes greatly in Bulgaria, for the total production, as is well-known, came last year to not more than 4250 kilos, of which about 720 kilos are still in the hands of speculators. The difference shows clearly what quantities of geranium oil are served up to the consumers under the name of rose oil. It may be mentioned here as a curiosity, that one Bulgarian merchant offers his oil under the absurd name of *Essence de Roses d'or*.

Large quantities of geranium oil have this year again been clandestinely imported, and have been prepared by distillation over roses. In Kazanlik alone the quantity is estimated at 560 kilos.

The roses have been bought in Kazanlik at 22½ to 25 centimes per kilo. In the villages the price was 15 to 20 centimes. For this reason more oil was distilled in the villages, whilst in the larger towns the dearer roses were employed on a large scale for the preparation of geranium oil.

For the rest, the Government is seriously considering steps for putting a stop to the adulteration of rose oil. The question is ripe, and the days of adulteration, which has ruined this beautiful and profitable industry, are counted. The present law, which prohibits the importation of geranium oil, is but a delusion, for it does not hurt those who mix geranium oil with rose oil, but only those in whose possession the pure geranium oil is found."

This report may be taken as representing in a general way the actual state of affairs. Since it was written, however, a severe financial crisis has come over Bulgaria, the effect of which is felt everywhere, from the largest financial institutions down to the small farmers, and which paralyses all enterprise. As a matter of fact, speculation in rose oil is considered a very dangerous matter by those who have an exact knowledge of the situation, as the rose plantations are constantly being enlarged, and next year's production, under favourable circumstances, might easily come up to about 6000 kilos.

All these considerations call for caution, and render a decline in the prices not at all impossible.

**Rose Oil, German.** As a portion of our rose fields, after ten year's cultivation, had to be ploughed up, and the new plantations have this year not yet supplied a tangible yield, the harvest of 1901 has given only half the usual result. As a consequence, the production of oil has also fallen behind that of the previous year.

After executing the orders booked in advance, we have about 12 kilos of our own distillate left, from which we continue to supply as long as we have any left in stock.

Owing to the greater yield of the distillation we have been able to reduce our price.

**Rose oil, artificial, "Schimmel & Co."** This excellent product has in a short time gained the favour of a very large circle of clients. It has an exquisite perfume; it fascinates by the delicacy as well as by the persistency of the odour, and possesses all the properties needed in a serious competitor of the Bulgarian oil. Its introduction has been materially assisted and promoted by the general distrust felt for Bulgarian rose oil, a distrust which increases more and more with every new sensational report from the producing districts. Under the circumstances there is certainly justification for the thought, whether it would not be better to buy, in the place of a doubtful natural product, — the consumption of which at the same time promotes its adulteration — an artificial product, whose composition is based upon scientific principles and is freely published, and which possesses practical properties of such a character that it deserves to be placed alongside the natural distillate.

**Rosemary Oil.** The distillation taking place in France in June and July, has given favourable results, so that a continuation of the present low prices may be relied upon. The reports on the distillation in Dalmatia, however, are unfavourable; the producers there ask higher prices. The Spanish distillate has now also become very well introduced, but it is to be regretted that it cannot be obtained more regularly in reliable quality.

**Rue Oil.** In his work on rue oil, of which we have given more details in our last Report, Thoms mentions, in addition to other derivatives of methyl-n-nonyl ketone produced by him, also the condensation product of the same with benzaldehyde,  $C_{18}H_{26}O$ . According to Thoms it has the form of small colourless scales, which are greasy to the touch, are readily soluble in alcohol, ether, and chloroform, and melt at 44 to 45°.

According to Carette<sup>1</sup>), who has prepared the same compound at about the same time, the melting point lies between 41 and 42°. Carette thus explains this difference in the melting points, that the crystals obtained by Thoms may possibly have contained traces of a polymeric condensation product of the ketone with benzaldehyde, which had also been prepared at the time by Carette, and which melts at 116°.

We have found that, by extracting oil of rue with 20 per cent sulphuric acid, a small quantity of a basic oil can be obtained, which, in solution has a blue fluorescence, and possesses a strong odour reminding of methyl anthranilate. As we suspected the presence of this compound, the basic oil was saponified with alcoholic potash, and the portions which could not be saponified were driven over with steam. These are characterised by an exceedingly strong, peculiar, odour. When acetic acid was added to the saponification liquor, an acid separated out which in solution had a blue fluorescence, and which was extracted with ether. This acid behaves like an amidoacid; it dissolves readily in dilute hydrochloric acid and soda, and it can be recrystallised from hot water. The crystals obtained from water had a melting point between 165 and 175°; after sublimating them in vacuo, the melting point could be brought up to 173°. The acid is consequently not anthranilic acid; probably it is identical with methylanthranilic acid, whose melting point lies about 178 to 179°. The material up to the present at our disposal was not sufficient for the production of the acid in the perfectly pure state.

On the strength of the available data, however, we feel justified in expressing the opinion, that the blue fluorescent base in oil of

<sup>1</sup>) Compt. rend. 131 (1900), 1125, and Journ. de Pharm. et Chim. VI. 13 (1901), 412.

rue is the methyl ester of methylanthranilic acid, i. e. the same body which was detected by us in larger quantity in oil of mandarins<sup>1)</sup>.

**Rue Oil, Algerian.** H. von Soden and K. Henle<sup>2)</sup> have published in the "Pharm. Zeitung" a communication on Algerian oil of rue, from which we abstract the following:—

The oil examined had a pale yellow colour; its odour was that of rue, with a distinct flavour reminding of certain ketones of the aliphatic series, such as methyl hexyl ketone. The specific gravity was 0.842, at 15°; the optical rotation  $-5^{\circ}$ , and the saponification number 64. The oil did not yet solidify at  $-15^{\circ}$ .

The principal constituent of Algerian rue oil was found to be methyl heptyl ketone, which was probably the normal compound, a question which, however, is still to be determined by further examinations. The following constants are given for the ketone:—

Specific gravity at 20° = 0.821.

Boiling point 193 to 194° at 740 mm.

Congealing point  $-15^{\circ 3)$ .

The semicarbazone produced from the methyl heptyl ketone forms small brilliant leaflets of the melting point 118 to 119°.

In addition to the ketone referred to, Algerian rue oil was also found to contain small quantities of methyl nonyl ketone and ester-like compounds, upon whose examination the authors are still engaged.

It can, however, already be stated, on the strength of the result of the examinations so far carried out, that Algerian rue oil is totally different from ordinary rue oil, both as regards the physical constants and the chemical composition.

The authors also correct in their communication the boiling point of methyl-n-nonyl ketone, which they give as 230 to 231° (740 mm), whilst others had found it at 224°.

**Sandalwood Oil (East Indian).** The use of this oil, both in medicine and in perfumery, makes such rapid progress, that we found it necessary to make special arrangements in our new Works for the manufacture on a large scale, which arrangements have answered exceedingly well. The distillation process has not only been considerably shortened, but has also been so much improved from a technical point of view, that the product may now be said to have reached the highest pitch of perfection.

The rumours about the monopoly, which were circulated in London early in the year and caused a great sensation, have not been confirmed, but, on the contrary, have been officially contradicted.

<sup>1)</sup> Report October 1900, 31.

<sup>2)</sup> Pharm. Ztg. 46 (1901), 277.

<sup>3)</sup> Compare the data by Thoms given in our Report of April 1901, 52.

In July last Mr. J. L. Pigot, Conservator of Forests in Mysore, requested us to contradict in a direct manner the English rumours mentioned in our April Report, by the publication of the following official notice:—

**Government of Mysore,  
Office of the Conservator of Forests in Mysore.**

Bangalore, 10th June 1901.

Notice is hereby given that sandalwood of all descriptions, including classes Nos 13 to 18, which were reserved from public sale in 1900, will be sold as usual by auction at the close of the current year. Details of the quantities to be offered for sale will be notified in due course.

(signed) B. Heerasingh,  
for Conservator of Forests in Mysore.

In further explanation, Mr. Pigot adds that the concession once granted to the East India Association, L<sup>d</sup>, for the exclusive rights to distil sandalwood in Mysore, has lapsed and will not be renewed.

It follows that in the sandalwood trade everything remains as before. The Government will generally be able to estimate the world's requirements with sufficient accuracy not to depress the value by excessive sales.

The value of the export of sandalwood from Bombay amounted:

in 1898/1899 to 160,182 Rupees  
against „ 1899/1900 „ 274,757 „

For a considerable time, and from many quarters, we have been requested to undertake ourselves the manufacture of sandalwood capsules on a large scale, so that our clients might be certain to receive our oil in the capsules and could guarantee this to their customers. Before we act upon this suggestion, we would propose that in such cases the firm supplying the capsules be asked to give a written guarantee, that their capsules are filled with Schimmel & Co.'s sandalwood oil, and we have no doubt that this will then be the case.

In a paper entitled „Contributions to the knowledge of East Indian sandalwood oil”<sup>1)</sup>, M. Potvliet draws attention to the fact, that the determination of the physical constants of the oil alone is never sufficient, but that the santalol-content should also be always determined, if the quality of the oil is to be judged. On the strength of examinations made by himself Potvliet declares, that it is quite possible to prepare mixtures of East Indian sandalwood oil with West Indian and cedarwood oil, which meet the ordinary requirements. Even the content of alcohol was in some cases more than 90 per cent.

<sup>1)</sup> “Sandalwood and sandalwood oil.” Pamphlet published by the Oranje Company, Amsterdam, May 1901.

The examination of numerous samples of personally distilled East Indian sandalwood oils showed, that in these the santalol-content generally fluctuates between 93.5 and 97.7 per cent, but in no case s less than 92.5 per cent.

According to Potvliet, genuine unadulterated East Indian sandalwood oil should satisfy the following requirements:—

Specific gravity at 15° = 0.975 to 0.985.

Optical rotation = — 17° to — 20°.

Soluble in 4 to 4.5 volumes of 70 per cent alcohol at 20°.

Santalol-content at least 92.5 per cent.

In connection herewith, Potvliet makes some further brief observations on the chemical composition of East Indian sandalwood oil, which, however, contain nothing new.

With regard to the solubility of East Indian sandalwood oil, the remark has been made from another side, that the requirements of the German Pharmacopœia, "that sandal oil should make a clear solution with 5 parts of dilute alcohol", cannot be complied with, even when the oil is perfectly unobjectionable.

Many persons may have come to a different conclusion when making repeated tests. This would be due to the fact, that the percentage of alcohol in the dilute spirit of the Pharmacopœia may fluctuate within one per cent by volume. And whereas sandalwood oil is soluble in five parts of 69 per cent alcohol, it will only make a cloudy mixture with alcohol of 68 per cent, which will not form a clear solution until at about 24°. This explains why occasionally a perfectly pure sandalwood oil may not appear to answer the solubility test of the German Pharmacopœia.

Under these circumstances it would certainly be advisable that the German Pharmacopœia should specify, for the solubility test of essential oils, the use of an alcohol of quite definite strength, for example 70 per cent by volume. This is all the more desirable, as the same difficulties as with sandalwood oil have been encountered with some lavender oils which otherwise were perfectly unobjectionable; similar occurrences would then be rendered impossible.

Less advisable appears to us the proposal<sup>1)</sup> made from another side, that for sandalwood oil the solution should be required to have a temperature of about 20 to 30°, whilst the "dilute alcohol" is retained as heretofore.

**Sandarac Oil.** The essential oil contained in sandarac resin was prepared some few years ago by Tschirch and Balzer<sup>2)</sup> by treating the non-pulverised resin with overheated steam. The yield obtained by these investigators was, however, so small, that an examination of the oil could not take place.

<sup>1)</sup> Pharm. Centralhalle N. F. 22 (1901), 566.

<sup>2)</sup> Archiv der Pharmacie 234 (1896), 310.

Th. A. Henry, during an investigation of the constituents of sandarac resins<sup>1)</sup>, has obtained the oil by a different process. He added to an alcoholic solution of the resin a slight excess of alcoholic potash solution, then distilled the alcohol off, dissolved the residue with water, and extracted the solution with ether. The oil remaining after removal of the ether was then immediately fractionated. The author has, unfortunately, given no particulars of the yield (which appears, however, not to have been very large), nor of the physical constants of the oil.

According to Henry, sandarac oil consists mainly of hydrocarbons; he detected in the low boiling fractions d-pinene ( $n_D + 18^\circ 27'$ ), identified by the nitrosochloride and the nitrolpiperidine. In the higher boiling fractions a body is found, which, after previous treatment with sodium, passes over between  $260$  and  $280^\circ$ , and which appears to belong to the class of diterpenes, according to its constants:  $d_{15}^{150} = 0.9386$ ;  $n_D = 1.5215$ ; it does not combine either with hydrochloric acid or with nitrosylchloride, or nitrogen trioxide.

**Spike Oil.** The result of the distillation which has just come to an end meets with general praise. For this reason the French producers are very accommodating, a fact which has led to our purchasing several large parcels. The consumption of this oil, either for perfuming soaps, or in the ceramic industry, increases from year to year.

**Star-anise Oil.** Contrary to all expectations and experience, the prices of this staple article have fallen without intermission, and have now arrived at a level never reached before. If, in spite of a price of  $4/6$  per lb., the oil is everywhere treated with indifference, there must have been an enormous production, and competition must begin to affect the sale of star-anise oil. In the case of essential oils, as in other matters, taste has undergone a change in the course of time, and it cannot have escaped those who know the inner workings as we do, that especially for the manufacture of condiments, for which hitherto star-anise oil had been employed, anethol, which has a distinctly greater purity and a finer taste, is now often used in its stead. It is a fact that the consumption of anethol grows at the expense of star-anise oil, and this factor should not be lost sight of in judging the value of the latter. But the downward tendency, which has now continued for several years, has also, naturally, stimulated speculation. In China a further decline was already considered impossible when the price was  $6/-$ ; since then, every transaction has led to loss. When the disposition is so dull, even the lowest quotation is too high.

<sup>1)</sup> Journ. Chem. Soc. 79 (1901), 1149.

**Vetiver Oil.** We have repeatedly taken the opportunity to call attention to the fact, that the vetiver oil distilled in Réunion differs considerably in its properties from that which we have distilled ourselves. In our Report of October 1897 we published a comparative examination of the two oils.

In respect of consistency, odour, density, rotation, and saponification number, the differences are striking; and in consequence of insufficient knowledge of the chemical composition of vetiver oil, it has, unfortunately, not yet been possible to determine whether the differences mentioned above must be attributed to adulteration of the oil distilled in Réunion, or whether perhaps fresh roots yield another distillate than dry ones.

E. Theulier<sup>1)</sup> has recently written a contribution to this question, without, however, assisting thereby in clearing the matter up. He examined an oil distilled at Grasse, and one obtained from Réunion. The former was more viscid than the latter, and had a stronger aroma; the oils further showed the following differences:—

	Oil distilled at Grasse	Oil obtained from Réunion
Specific gravity at 20° . . . . .	1.0091	0.986
Optical rotation at 20° . . . . .	+ 35° 10'	+ 28°
Saponification number . . . . .	44.40	18.28
Acid number . . . . .	32.48	6.16
Ester number . . . . .	11.92	12.12

The solubility in 80 per cent alcohol was the same for both oils, i. e. 1 in 1.5.

Fractional distillation of both oils, under 25 mm. pressure, revealed further differences, both with regard to the limits of temperature within which the oils passed over, and to the optical rotation and the percentage of acid of the individual fractions. But the specific gravities, solubility and ester-content of the corresponding fractions of both oils differed only little.

Theulier believes that the samples of vetiver oil examined contain the same constituents, but in different proportions, and that moreover the dried root, owing to processes of oxidation, contains other products which yield higher-boiling fractions, which products are absent in the Réunion oil distilled from the fresh root. Theulier thinks that the difference in the properties and composition of the two oils may also be due to badly conducted distillation in Réunion.

A fact of practical value is, that the vetiver oil distilled by us has a much more intense and pleasant odour, and fully justifies the higher selling price.

<sup>1)</sup> Bull. Soc. chim. III. 25 (1901), 454.

**Wintergreen Oil.** The reports from New York continue to give unfavourable news. The production has fallen off considerably, and the price would have at least doubled, if the competition of the artificial oil had not put a certain limit to the increase in the quotations. A change in the present situation is not to be expected in the immediate future.

The "Oil, Paint and Drug Reporter" publishes, in its issue of September, a statistical table of the prices of wintergreen oil during the last ten years, which we reproduce here:—

	1891		1892		1893		1894		1895	
	H.	L.	H.	L.	H.	L.	H.	L.	H.	L.
January . . . . .	1.70	1.70	1.75	1.75	1.70	1.70	1.45	1.45	1.35	1.35
February . . . . .	1.70	1.70	1.75	1.75	1.70	1.70	1.40	1.40	1.35	1.25
March . . . . .	1.70	1.70	1.75	1.75	1.67 <sup>1</sup> / <sub>2</sub>	1.67 <sup>1</sup> / <sub>2</sub>	1.45	1.45	1.25	1.25
April . . . . .	1.70	1.70	1.80	1.75	1.67 <sup>1</sup> / <sub>2</sub>	1.67 <sup>1</sup> / <sub>2</sub>	1.45	1.45	1.25	1.25
May . . . . .	1.70	1.70	1.80	1.80	1.67 <sup>1</sup> / <sub>2</sub>	1.67 <sup>1</sup> / <sub>2</sub>	1.45	1.45	1.35	1.25
June . . . . .	1.70	1.70	1.75	1.75	1.67 <sup>1</sup> / <sub>2</sub>	1.67 <sup>1</sup> / <sub>2</sub>	1.45	1.40	1.35	1.30
July . . . . .	1.70	1.70	1.75	1.75	1.67 <sup>1</sup> / <sub>2</sub>	1.67 <sup>1</sup> / <sub>2</sub>	1.40	1.40	1.30	1.30
August . . . . .	1.75	1.70	1.75	1.75	1.67 <sup>1</sup> / <sub>2</sub>	1.67 <sup>1</sup> / <sub>2</sub>	1.30	1.30	1.30	1.20
September . . . . .	1.85	1.75	1.75	1.70	1.67 <sup>1</sup> / <sub>2</sub>	1.67 <sup>1</sup> / <sub>2</sub>	1.30	1.30	1.20	1.20
October . . . . .	1.80	1.80	1.70	1.70	1.67 <sup>1</sup> / <sub>2</sub>	1.60	1.30	1.30	1.20	1.20
November . . . . .	1.80	1.75	1.70	1.70	1.60	1.60	1.35	1.30	1.20	1.20
December . . . . .	1.75	1.75	1.70	1.70	1.60	1.45	1.35	1.35	1.20	1.20
Average for the year	1.85	1.70	1.80	1.70	1.70	1.45	1.45	1.30	1.35	1.20

	1896		1897		1898		1899		1900	
	H.	L.	H.	L.	H.	L.	H.	L.	H.	L.
January . . . . .	1.20	1.20	1.20	1.15	1.—	1.—	1.—	1.—	2.50	2.—
February . . . . .	1.25	1.20	1.15	1.15	1.—	1.—	1.—	1.—	1.95	1.75
March . . . . .	1.25	1.20	1.15	1.15	1.—	1.—	1.25	1.—	1.75	1.50
April . . . . .	1.20	1.20	1.15	1.10	1.—	1.—	1.20	1.20	1.50	1.50
May . . . . .	1.20	1.20	1.10	1.10	1.—	1.—	1.20	1.15	1.50	1.50
June . . . . .	1.20	1.20	1.10	1.05	1.—	1.—	1.15	1.15	1.50	1.40
July . . . . .	1.20	1.20	1.10	1.10	1.—	1.—	1.25	1.15	1.40	1.40
August . . . . .	1.20	1.20	1.10	1.10	0.95	0.95	1.35	1.25	1.40	1.35
September . . . . .	1.20	1.20	1.10	1.10	0.95	0.95	1.40	1.35	1.35	1.30
October . . . . .	1.20	1.20	1.10	1.10	0.95	0.95	2.—	1.40	1.50	1.30
November . . . . .	1.20	1.20	1.10	1.05	0.95	0.95	2.50	2.25	1.75	1.50
December . . . . .	1.20	1.20	1.05	1.—	1.—	0.95	2.50	2.50	1.75	1.75
Average for the year	1.25	1.20	1.20	1.—	1.—	0.95	2.50	1.—	2.50	1.30

These figures show, that the highest quotation was \$ 2.50, in 1899, and the lowest \$ 0.95, in 1898. The normal average price is approximately that quoted now.

**Wormwood Oil.** Fine French distillates are scarce, and are held for higher prices. American oil was exceedingly difficult to obtain in reliable quality. Since 1898 the production has continually declined, and this year it is so small, that nothing can be spared for export. One of our friends, a distiller in Wayne County, has obtained only 125 lbs. of oil from 107 acres of herb. Other growers

in the territories of Michigan and Indiana have gathered only one-fifth of last year's harvest. We are informed that \$ 7.— to \$ 8.50 per lb. have been paid, which would be equal to 63—75 Marks per kilo. Under these circumstances the reintroduction of American oil is out of the question.

**Ylang-Ylang Oil.** The preferred brand "Sartorius" (the exclusive sale of which remains now as before in our hands), was out of stock for several weeks, but a small consignment has just reached us, and 10 cases more are at this moment on the way from Marseilles. The affairs in Manila are at last again acquiring a normal character. Communication with the interior has been reopened, and it is now possible to obtain regular supplies of flowers and to take up the distillation on the same scale as before, so that the calamity may now be fairly considered as at an end.

We have already previously mentioned, and repeatedly observed, that eugenol belongs to the constituents of cananga oil<sup>1)</sup>. Of ylang-ylang oil, which is related to cananga oil, it has only been ascertained that it gives colour-reactions with ferric chloride, which points to the presence of phenols. We have found that isoeugenol is present among the phenols of ylang-ylang oil, a fact which deserves attention, as it is the first time that this phenol has been discovered in nature. The phenols were removed from ylang-ylang oil with dilute soda solution, their ethereal solution shaken with sodium carbonate solution in order to remove any free acids present, and the oil freed from ether was fractionated in vacuo. It distilled at 12 mm. pressure from 115 to 165°, the bulk between 142 and 147°. This fraction had the odour of isoeugenol, and with ferric chloride produced a blueish green coloration. By Zeisel's method methoxyl groups could be detected in the fraction; with benzoyl chloride and soda solution a benzoyl compound was formed, melting at 103 to 104°. The benzoyl compound obtained from artificial isoeugenol had the same melting point. The mixture of the two bodies, when melted, behaved in the same manner. A portion of the isoeugenol from ylang-ylang oil was converted with acethydride into the acetyl compound, which melted at 79—80°. The same melting point is given by Tiemann<sup>2)</sup> for acetyl isoeugenol. For further proof another portion of the isoeugenol fraction from ylang-ylang oil was shaken with dimethyl sulphate and potash solution, and, to the ethereal solution of the methyl isoeugenol thus formed, bromine was added until nothing more was absorbed. On evaporation of the ether crystals separated out, which, after washing with ethyl acetate and

1) Report April 1899, 10.

2) Berliner Berichte 24 (1891), 2873.

recrystallisation from benzene and petroleum ether, melted at 101 to 102°.

The compound thus obtained is dibromide of the methyl isoeugenol whose melting point Ciamician and Silber<sup>1)</sup> have also found at 101 to 102°. In the lower-boiling phenol fractions of ylang-ylang oil creosol appears to be present. The acids abstracted from the crude phenols with soda solution were found to be a mixture of benzoic and salicylic acids, melting at 116°. The last-named acid has also been detected by us in cananga oil. In order to separate these acids, their mixture was esterified, and the benzoic acid ester was freed from the methyl salicylate by treating with soda solution. The salicylic acid recovered from the ester by saponification had the melting point 155°, and on addition of ferric chloride it showed the characteristic blue-violet colour-reaction. Both acids, combined partly with methyl, partly with benzyl alcohols, are present in the oil in the form of esters.

In addition to these bodies, we have discovered some more constituents of ylang-ylang oil, which have an important effect on the formation of the aroma of this oil.

For the proper protection of this invention we have on the 23<sup>d</sup> September of this year, lodged an application for a patent.

With regard to the terpenes suspected in ylang-ylang and cananga oils, nothing certain has up to now become known. We have obtained from cananga oil, by fractional distillation, a very small quantity of a terpene boiling at 160°, which was found to be dextro-pinene with the optical rotation +16°20'. It was identified in the usual manner by conversion into its nitrosochloride, and its nitrobenzylamine compound melting at 123°. In addition to the above there is present, both in cananga and in ylang-ylang oil, a body with a peculiar odour, boiling at 145 to 148°, which appears to be a ketone, about whose properties we reserve further communications.

**Ylang-Ylang Oil, artificial, "Schimmel & Co."** As is shown by the foregoing notes on the work continued in our laboratories, our chemists have discovered a further constituent of natural ylang-ylang oil, hitherto unknown, viz., isoeugenol, and they have thereby made an important step towards perfecting the artificial product.

Our newly discovered constituents bring the latter, as regards quality, so close to the natural oil, that it can now scarcely be distinguished from the finest brands, and forms a complete substitute for the natural product.

We would most strongly advise our clients to obtain samples of our present product, in order to convince themselves of the important improvement recently made in the quality.

<sup>1)</sup> Berliner Berichte 23 (1890), 1167.

The *Revue des cultures coloniales*<sup>1)</sup> contains an article, well worth reading, by E. Heckel, director of the Institut Colonial at Marseilles, entitled *Notes sur les plantes à parfums et sur le développement possible de cette industrie en Nouvelle-Calédonie*.

The author argues strongly in favour of the idea of developing, in the French colony New Caledonia, the industry of producing floral odours which has attained such a high degree of prosperity in Cannes and Grasse. There, all conditions are present which would warrant a successful issue. The authorities of the penal settlement on the Ile des Pins could at least carry out practical experiments at small expense, as female labour is abundant. It could only be in the interest of the Government to employ this labour, and the free colonials would soon imitate the first trials. As long ago as 1888, M. Bompard gave expression to this idea, and advised the cultivation of orange trees. If at that time the suggestion had been acted upon, the plantations would now be fully developed, and it would be possible to look back upon decisive results. As a matter of fact, the cultivation of the orange tree is the one which promises the most remunerative results in perfumery. The South of France produces only about 465,000 litres of orange flower water, and more than a million litres are exported, not including the quantity used in France itself. A large proportion is made from the leaves, but the properties of this product are not of the same value as those of the genuine article. France imports also every year, for Paris alone, essences, perfumed oils and fats, of a total value of 5 million francs. This figure is given by the Chamber of commerce of Paris. It will therefore not appear exaggerated, if the imports for the whole of France are taken at a value of 12 million francs. New Caledonia could easily produce a large proportion of these essences and perfumed fats, which form the basis of the perfumery industry, and of which the production does not offer great technical difficulties.

The following three processes might be suitable for New Caledonia : enfleurage, maceration, and distillation.

Ben oil, which used to be employed largely for enfleurage, also in France, can be produced with facility in New Caledonia from the indigenous *Moringa pterygosperma* Gaertn. Ben oil is superior to olive oil, now much used, chiefly because it does not readily become rancid; the only reason for its practical disappearance from the French market is its high price. The products made with ben oil should undoubtedly be preferred.

The enfleurage method can be carried on without large means and is especially adapted for flowers whose aroma is unable to bear great heat. Flannel cloths are saturated with ben oil and stretched on frames, and flowers strewn over them. The flowers remain on

<sup>1)</sup> Vol. VIII (1901), 258.

the cloth for 50 to 60 hours, until they have imparted the whole of their aroma to the oil. When the fatty oil is saturated with the floral odour it is recovered from the cloths by pressure.

The maceration process can also be carried on without large expenditure, and it would be assisted by the proximity of Australia, which has such an abundance of cattle that it can easily supply the animal fat required for the maceration. Moreover, this continent would offer a good market for the products of this industry. The fact that New Caledonia is so remote from France is not of much consequence for goods of small bulk and high value. The author then mentions a number of plants, which would specially come into consideration for New Caledonia.

In the first place come the agrumens (*Auranticeæ*). The three most important species, the sweet and bitter orange (*Citrus Aurantium* L. and *Citrus Bigaradia* Risso) and the mandarin (*Citrus madurensis* Loureiro) have already been introduced in New Caledonia in 1858, since when they have propagated and are well acclimatised. The lemon and *Citrus Histrix* DC., whose oil compares favourably with that of the bergamot, also thrive there. The latter would easily become naturalised. Other important species are the *Eucalyptus citriodora* Hook., introduced in 1890, and the cassie (*Acacia Farnesiana* Willd.) originating from India. This shrub, so exceedingly important for the perfumery industry, has propagated to such an extent, that it has almost become a plague for the agriculture. At the author's suggestion, the *Acacia decurrens* Willd. has also been planted since 1890. Indigenous plants are moreover *Acacia Lebbeck* Willd. and *Acacia spirorbis* Labill. which are as yet unknown to the perfumery trade. The following may also be mentioned among the large number of aromatic plants given by Heckel, which are found in New Caledonia and thrive there luxuriously: jasmine (*Jasminum grandiflorum* L.), geranium (*Geranium capitatum* L.), heliotrope (*Heliotropium peruvianum* L.), vetiver (*Andropogon muricatus* Retz.), and *Andropogon Schoenanthus* L.

The author does not share the opinion which prevails in certain political circles in France, that the industrial development of the colonies should be resisted. In this case, those engaged in industry in Cannes and Grasse could make New Caledonia an excellent "branch business" of Southern France.

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**Kauri Copal.** A. Tschirch and B. Niederstadt<sup>1)</sup> have communicated an essay on the composition of kauri copal from *Dammara australis* and the resin of *Pinus silvestris*. The New Zealand kauri copal examined consists partly of free acids, among them

<sup>1)</sup> Archiv der Pharm. 239 (1901) 145—181.

the crystallising acid  $C_{10}H_{16}O_2$ , kauric acid, which is obtained by shaking an ethereal solution of the copal with 1 per cent aqueous ammonium carbonate. By treating the ethereal solution with 1 per cent aqueous sodium carbonate, two amorphous isomeric acids  $C_{12}H_{20}O_2$ ,  $\alpha$ - and  $\beta$ -kaurollic acids, could be abstracted. From the ethereal solution now remaining 1 per cent aqueous potash extracts two more amorphous acids, kaurinolic acid  $C_{17}H_{34}O_2$  and kaunolic acid  $C_{12}H_{24}O_2$ . The residue left after removal of all these acids, yielded on steam distillation an essential oil possessing a pleasant odour. The specific gravity of the latter was 0.835, at  $15^\circ$ ; the boiling point was between  $150$  and  $160^\circ$ , mostly at  $156$ — $160^\circ$ .

An ethereal solution of a resin of *Pinus silvestris* originating from Finland, when extracted with sodium carbonate, yielded the crystalline acid  $C_{14}H_{20}O_2$ , silveolic acid, and two amorphous acids  $\alpha$ -silvinolic acid  $C_{15}H_{26}O_2$  and  $\beta$ -silvinolic acid  $C_{14}H_{24}O_2$ . The resin freed from the acids contained an essential oil having a pleasant odour, which was obtained from the resin by steam distillation. Its specific gravity was 0.840; the boiling point was between  $155$  and  $163^\circ$ .

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### Notes on recent scientific work concerning terpenes and terpene derivatives.

E. Charabot and A. Hébert<sup>1)</sup> have made experiments respecting the process by which ester is formed in the plant, from which trials the authors draw the following conclusions: The formation of ester in the plant takes place by the direct action of acids on alcohols; it is favoured by a special agent which has a dehydrating action. This is proved, both by the earlier researches<sup>2)</sup> by Charabot on the development of terpene compounds, and by the following observations:—

1. If acetic acid alone acts upon linalool, this alcohol is esterified much more slowly than is the case in the plant.
2. Those terpene alcohols which are most readily esterified under the influence of a given acid, are also those, of which the plant contains the largest quantity combined with that acid.
3. For one and the same terpene alcohol, the acid which combines most readily with that alcohol, is also the one whose ester is present in the plant in the largest quantity.
4. If two alcohols occur together in a plant, the acid during the process of esterification divides itself between those two alcohols.

<sup>1)</sup> Compt. rend. 133 (1901), 390.

<sup>2)</sup> Compare our Report October 1900, 66.

The special agent co-operating in the formation of esters is, according to Charabot and Hébert, nothing but a diastase, which exerts its dehydrating action inside the chlorophyll.

### Hydrocarbons.

F. W. Semmler<sup>1)</sup> has supplied a work of more general interest for the terpene chemistry; he discusses in it the conditions which may occur, when water, hydrohalogen, ammonia, &c., are split off from compounds of the terpene series. All these abstractions can occur in such manner, that either a double linkage is produced, or else a new ring formed. The conditions become very complicated when acids are used in the process (as for example when water is split off from alcohols), as in such case the double linkage may become displaced, or disruption of the primary formed rings may occur. They are more simple if the crude material consists of halogen compounds or amines, for in such cases it is a question of neutral or alkaline media, with which displacement of the double linkage is precluded, and disruption of a primary formed ring is only then possible, when a high temperature is required to perform the reaction. Another fact which complicates the abstraction of water from terpene compounds is, that under certain conditions, as, for example, with terpin, it occurs in more than two directions, whereby double linkages may be formed not only inside the ring, but also from the latter towards the side chains. Stereometric conditions clearly decide whether the abstraction takes place one way or the other; Semmler demonstrates this individually with numerous examples.

Pinene. In our Report of April 1901, p. 62, we pointed out, that for the purpose of determining the constitution of pinonic acid, it would be a matter of great importance to establish the atomic structure of isocamphoronic acid. We quoted for this acid two formulæ, of which, as we mentioned, "the former is due to Tiemann, and the latter to v. Baeyer". We would avail ourselves of this opportunity to state, that it would be more in agreement with the facts, if Bredt's name were substituted for that of Tiemann, for it was the first-named investigator<sup>2)</sup> to whom the chemistry of camphor owes so much, who has taken the first-mentioned formula for isocamphoronic acid into consideration before anyone else, and that nearly two years earlier than Tiemann. The only point of difference between the formulæ of the two investigators is their representation on paper: the arrangement of the atoms is the same in both.

<sup>1)</sup> Berliner Berichte 34 (1901), 708.

<sup>2)</sup> Compare Liebig's Annalen 289 (1896) 19, and 314 (1901), 394.

On the question of artificial camphor and of camphene we have before us a short article<sup>1)</sup> by J. Kondakow. He discusses therein the views of different scientists, especially on the character of pinene hydrochloride, — whether this is to be considered as a secondary or as a tertiary compound, — without, however, solving the question in a satisfactory manner.

Camphene. N. Demjanow<sup>2)</sup> reports on the action of nitric acid anhydride on camphene. If camphene and nitric acid anhydride, both dissolved in chloroform, are brought together while the temperature is considerably reduced, there are soon formed, in the residue remaining after evaporation of the solvent, crystals of a compound  $C_8H_{14}:C(ONO_2)CO_2H$  of the melting point 140 to 141°, which has an acid-like character and yields salts. When heated with concentrated potash solution, or when reduced by means of tin and hydrochloric acid, an acid  $C_{10}H_{14}O_2$  is formed, which is identical with dehydrocamphenylic acid, melting point 147.5 to 148°, obtained by Wagner and Majewski from camphenylic acid. Demjanow believes that from camphene and nitric acid anhydride, in the first place probably the nitric ester of camphene glycol  $C_{10}H_{16}O_6N_2$  is formed, which is then converted into the acid referred to:  $C_8H_{14}:C(ONO_2)CO_2H$ . The author considers the result of his examination a confirmation of Wagner's "isobornylene" formula.

Fenchene. Wallach's 51<sup>st</sup> treatise<sup>3)</sup> gives some noteworthy particulars on the oxidation products of fenchene. The progress of the examination of the isomeric fenchenes has rendered it probable, that, in addition to the two hydrocarbons<sup>4)</sup> previously described by Wallach, a third fenchene may be formed when fenchyl alcohol, by way of the chloride, is converted into the hydrocarbon  $C_{10}H_{16}$ . It is therefore possible that the crude fenchene contains at least three hydrocarbons; of these three, one is readily oxidised, whilst the other two are only attacked with difficulty by potassium permanganate. If a mixture of fenchenes is oxidised, it may easily happen that from the salts of the oxyacids produced, an acid mixture is obtained, which, even after repeated recrystallisation, has a fairly uniform appearance and a constant melting point, and which by conversion into the barium salt and its fractional crystallisation, can be separated into D-l- and D-d-oxyfenchenic acid of the correct melting point. If, however, the fenchene contains very readily oxidisable hydrocarbons, the potassium salts formed during the oxidation are frequently syrup-like, and mineral

1) Chemiker-Zeitung 25 (1901), 609.

2) Chemisches Centralblatt 1901, II. 346.

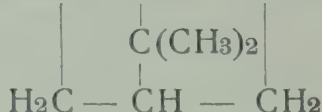
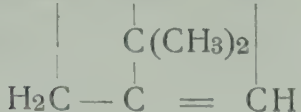
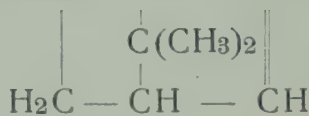
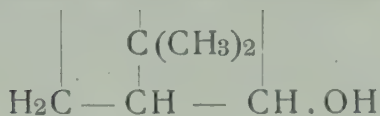
3) Liebig's Annalen 315 (1901), 279.

4) Compare our Report of April 1899, p. 49.

acids separate from them oily instead of solid acids, which represent somewhat complicated mixtures; the higher-boiling fractions contain, besides D-l- and D-d-oxyfenchenic acid, a further product of oxidation of one of the fenchenes, viz., a ketonic acid  $C_8H_{12}O_3$ , whose semicarbazone melts at  $210^\circ$ .

The fact that, when water is split off from fenchyl alcohol, several hydrocarbons  $C_{10}H_{16}$  are formed simultaneously, has rendered the investigation much more difficult, and has made the progress very slow. For some of these fenchenes, however, strongly characterised derivatives have now been discovered, as, for example, for D-l-fenchene D-l-oxyfenchenic acid and its product of oxidation, D-d-fenchocamphorone; for D-d-fenchene D-d-oxyfenchenic acid, and D-l-fenchocamphorone. By means of these derivatives these hydrocarbons can also be detected in mixtures.

Further on Wallach discusses the constitution of the fenchenes from D-l-fenchyl alcohol, for which come into consideration, taking as a basis formulæ I, in the first place formulæ II and III, perhaps also IV — excluding further formulæ due to constitutional changes:—



Formula III might possibly apply to the hydrocarbon present in the crude fenchene, which yields the ketonic acid with eight carbon atoms, whilst for D-l-fenchene IV might perhaps be preferred. In the meantime the question of the constitution of D-d-fenchene must remain unanswered; this matter can only be cleared up completely by the further examination of the products of oxidation. The experimental basis necessary for a statement regarding the relation of isofenchyl alcohol to fenchyl alcohol and to the fenchenes, is also wanting at this moment.

Phellandrene. While engaged on the examination of the sesquiterpene of ginger oil, Oswald Schreiner<sup>1)</sup> observed that this hydrocarbon forms a nitrite melting at  $97$  to  $98^\circ$ , which in its appearance bears a slight resemblance to phellandrene nitrite. As the

<sup>1)</sup> Note on phellandrene nitrite and phellandrene-containing oils. *Pharmaceutical Archives* 4 (1901), 90.

statements on the melting point of phellandrene nitrite, which are found in the literature, fluctuate between 94 and 105°, and as in most cases when this compound was obtained in testing essential oils for phellandrene, it was not submitted to a closer examination, the author has made a further study of this reaction, which is of so much importance for the detection of phellandrene. He prepared phellandrene nitrite from a *lævogyre* fraction of eucalyptus oil by the usual process. The crude nitrite was rapidly dissolved in boiling ethyl acetate, and then cooled in ice-water. When the solution had solidified, the crystalline mass was filtered off; when washed with ethyl acetate it showed immediately the constant melting point 120 to 121°. From the mother liquor crystals having melting points 110 to 111°, 105 to 106°, and 100 to 101°, were obtained by precipitation with 60 per cent alcohol, by the method recommended by Bertram and Walbaum<sup>1)</sup>. The optical rotation of the different yields varied between +123° and -36°, whereas the crude product showed +28.5°. The crude nitrite could, therefore, apparently be separated into a higher-melting dextrogyrate, and a lower-melting *lævogyrate* fraction. The same had already been observed by Gilde-meister and Stephan<sup>2)</sup>, with regard to the optical rotation, in the case of a phellandrene nitrite from oil of schinus. By repeated fractional crystallisation Schreiner obtained finally two compounds differing both in melting points and in the form of their crystals. The one melting at 120° forms well-developed needles, the other compound, melting at 105 to 106°, crystalline masses grouped in the form of stars. This separation of phellandrene nitrite into two compounds whose melting points are so different, explains the uncertain and low statements, which are met with in the literature on the subject of the melting point of phellandrene nitrite. The relationship between these two compounds is a matter still to be cleared up. It follows, however, from the foregoing, that the test for phellandrene in essential oils by the method hitherto in use is not sufficient, and that the numerous statements of the detection of this terpene do not give a definite guarantee of its actual presence.

The sesquiterpene of ginger oil yields a nitrosite melting at 97°. Bertram and Walbaum<sup>3)</sup> obtained from the lower-boiling fractions of the same oil a nitrite melting at 102°, which, according to the views then accepted, had to be considered as phellandrene nitrite. Schreiner also obtained this compound, and could bring the melting point by recrystallisation to 105°. Lack of material made it impossible to decide whether this compound completely agrees with the nitrite melting at 105°, obtained by fractional crystallisation from the

1) Archiv d. Pharm. 231 (1893), 298.

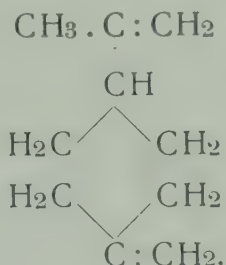
2) Ibidem 235 (1897), 591.

3) Journ. f. prakt. Chemie, N. F. 49 (1894), 18.

crude phellandrene nitrite. In any case it is not identical with zingiberene nitrosite obtained from the higher-boiling fractions of ginger oil.

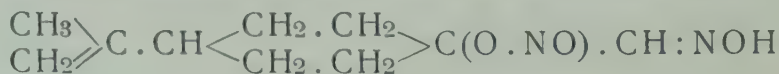
Note. We have repeated the above mentioned tests, and are in a position to confirm completely the statements made by Schreiner. It may also be recorded that at an earlier date Wilhelm Biltz (Thesis, Greifswald, 1898, p. 16) had already used a preparation for the determination of the molecular weight of phellandrene nitrite, which had the melting point 115 to 116°; such a high melting point had not been observed before.

Terpinene. The abstraction of water from dihydrocarveol by dilute sulphuric acid, and of ammonia from dihydrocarvylamine, leads chiefly to terpinene. Semmler<sup>1)</sup> has recently given the following constitution formula to this hydrocarbon:—



He therefore considers it as the limonene of the pseudo-class of terpenes.

He supports this conjecture especially thus, that terpinene nitrite — which he considers an aldoxime of the formula:—



on reduction yields, besides cymene, a hydrocarbon  $\text{C}_9\text{H}_{14}$  (boiling point 160 to 164°) which is a low homologue of the terpenes, and which could only have originated from the carbon atomic skeleton of terpinene by the loss of one carbon atom. This view of the constitution of terpinene is confirmed by the fact, that the hitherto known representatives of the pseudo-class of terpenes, like terpinene, react with Beckmann's solution. For this reason Semmler considers the latter a characteristic reagent with the pseudo-terpenes, pseudo-terpene alcohols, &c.

Thujene. Tschugaeff<sup>2)</sup> has continued his examination of thujene, and has endeavoured to prepare this hydrocarbon, which he regards as bicyclic, by other means than by the dry distillation of the methyl thujylxanthate. For this purpose he started from thujylamine, which Wallach and Semmler had previously also used

<sup>1)</sup> Berliner Berichte 34 (1901), 713.

<sup>2)</sup> Ibidem 34 (1901), 2279.

as material for the preparation of their thujene (or, according to Tschugaeff, isothujene); but instead of distilling its hydrochloride, he employed the method of exhaustive methylation, so as to prevent constitutional changes as far as possible.

Degradation by exhaustive methylation has already proved an excellent help in determining the constitution of several alkaloids, — recently again in degrading the bases of the tropine series; but this method has not been used on compounds of the terpene series, excepting in the single case when Wallach employed it for preparing a menthene from menthylamine. For this reason there are no data showing whether or not the use of this method also brings about molecular rearrangements in terpene derivatives.

The thujylamine required by Tschugaeff for this experiment was prepared by him by reducing thujonoxime with sodium and alcohol. The trimethylthujylammonium iodide formed by the action of an excess of methyl iodide and potash on thujylamine, was converted in the usual manner into the ammonium hydroxide, and the latter submitted to dry distillation. This yielded, though only in very small quantity, a hydrocarbon identical with that obtained from methyl thujylxanthate which has been described on a previous occasion, and from which it differed only in the rotatory power.

Tschugaeff therefore arrives at the conclusion, that the method of exhaustive methylation represents a means of producing unsaturated hydrocarbons, a process in which no formation of isomers is promoted.

### Ketones.

Fenchone. Wallach's 51<sup>st</sup> treatise on terpenes and essential oils<sup>1)</sup> supplies contributions to the knowledge of fenchone.

The by-products formed during the preparation of fenchocarbonic acid from fenchone, contain oils having, even in vacuo, very high boiling points, from which, after removal of the most volatile portions by steam distillation, upon prolonged standing crystals separate out, which after purification melt at 122°. Whether they have the composition of a difenchone, or represent the pinakone of fenchone, could not be definitely ascertained.

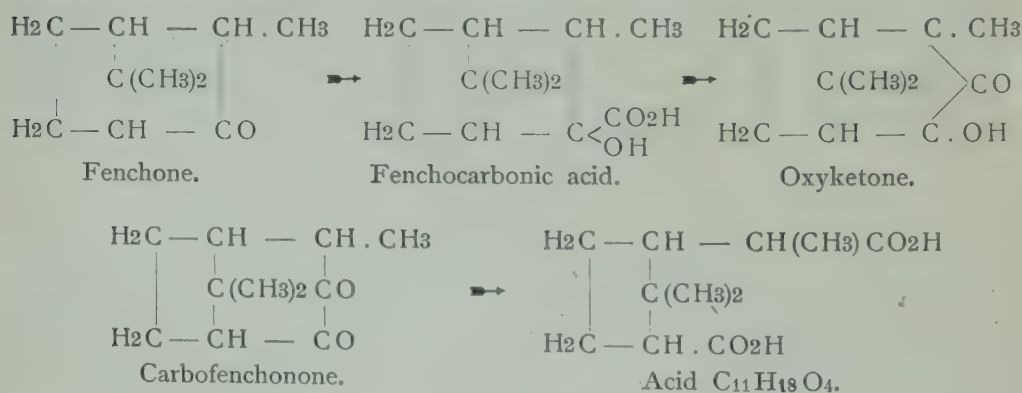
The yellow compound  $C_{11}H_{16}O_2$ , formed in the dry distillation of the lead salt of fenchocarbonic acid, which had hitherto been designated as oxycarbofenchonone, must be considered as o-diketone, as it yields, besides the already known monoxime, also a dioxime; for this reason it is now called carbofenchonone. With zinc dust and glacial acetic acid it is reduced into a colourless compound  $C_{11}H_{18}O_2$ , but treatment with sodium and amylic alcohol, on the contrary, changes it considerably.

<sup>1)</sup> Liebig's Annalen 315 (1901), 273.

Wallach further confirms Cockburn's statement that fencholene nitrile yields two isomeric acids. The brominated lactone  $C_{10}H_{15}O_2Br$  produced by the action of a solution of hypobromite on fencholenic acid, which has been described as characteristic of the latter, is formed both from the solid and from the liquid fencholenic acid. The melting point of the compound obtained from the  $\alpha$ -acid lies about  $76^\circ$ , that of the lactone from the  $\beta$ -acid about  $80^\circ$ .

In a theoretical conclusion the author rejects the objection raised by Marsh, that from the formula for fenchone recently drawn up by Wallach, the formation of as.-acetoxylol by concentrated sulphuric acid could not be explained. He does not consider the conversion of fenchone into acetoxylol as a simple reaction, the more so, as camphor, when treated with sulphuric acid yields the same acetoxylol; he believes that sulphuric acid has not only a dehydrating action on fenchone, but also effects a conversion and oxidation.

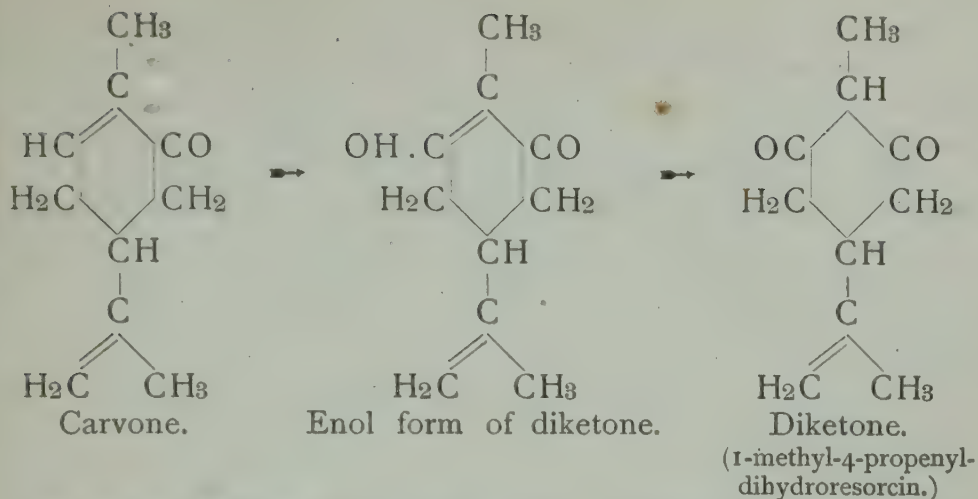
The derivatives of fenchocarbonic acid can be traced without difficulty from the fenchone formula employed by Wallach; in the first place fenchocarbonic acid is converted into an oxyketone, which changes into a diketone, carbofenchonone; oxidation converts the latter into an acid  $C_{11}H_{18}O_4$  isomeric with homocamphoric acid.



Carvone. C. Harries<sup>1)</sup> reports on the formation of a diketone  $C_{10}H_{14}O_2$  of the melting point  $185$  to  $187^\circ$  from carvone, which occurs when carvone is shaken for some time with baryta water to which a little methyl alcohol has been added. The author had obtained the same diketone previously by oxidation of the oxaminocarvoxime<sup>2)</sup>. From this the process of the oxidation of carvone into diketone might be represented by the following formulas:—

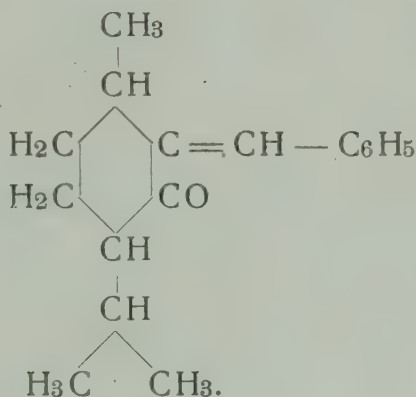
<sup>1)</sup> Berliner Berichte 34 (1901), 2105.

<sup>2)</sup> Ibidem 31 (1898), 1812.



A small quantity of a body with a pleasant odour like strawberries, is formed as a by-product in the carvone oxidation.

**Menthone.** According to Martine<sup>1)</sup> the action of benzaldehyde on sodium menthylate occurs in a manner analogous with the condensation of sodium bornylate with benzaldehyde, which was first carried out by Haller<sup>2)</sup>; benzylidene menthone is thereby formed, thus:—



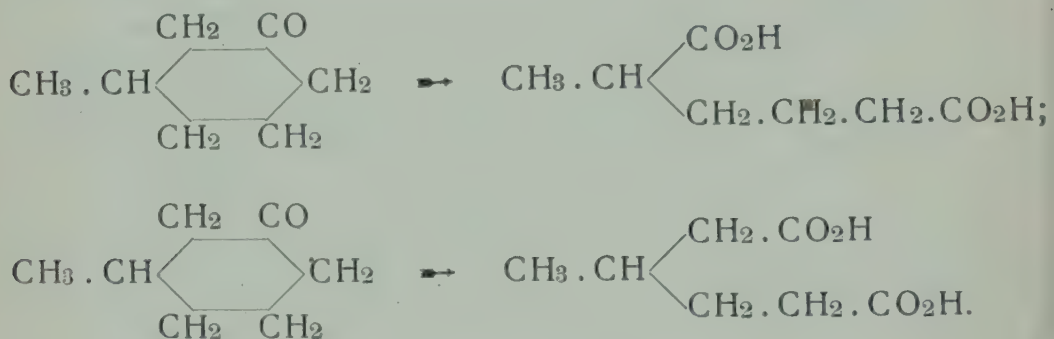
This has a boiling point of 195 to 196° (15 mm.) and yields, on treatment with concentrated HBr-solution in glacial acetic acid, the corresponding hydrobromide of the melting point 115°. For the d-benzylidene menthone regenerated therefrom,  $[\alpha]_D$  was found = +22.8 to 24.3°. The same d-benzylidene menthone is obtained by Wallach's<sup>3)</sup> method from l- and d-menthone, and by Haller's process also from l- and d-sodium menthone. An l-benzylidene menthone appears to be formed in the condensation of benzaldehyde both with sodium menthylate and with sodium menthone.

<sup>1)</sup> Compt. rend. 133 (1901), 41.

<sup>2)</sup> Ibidem 113 (1891), 22 and 130 (1900), 688.

<sup>3)</sup> Berliner Berichte 29 (1896), 1599.

**Pulegone.** According to Semmler, pulegone, on oxidation with potassium permanganate or chromic acid mixture, yields acetone and  $\beta$ -methyladipic acid; subsequently Wallach has proved that pulegone, on being heated with water to  $250^{\circ}$ , is readily split up into acetone and  $\beta$ -methylhexanone. But whilst in the case of pulegone, on account of the situation of the double linkage, only one oxidation process is possible, namely that by which  $\beta$ -methyladipic acid is formed, methylhexanone could yield either  $\alpha$ - or  $\beta$ -methyladipic acid, according to the point of attack of the oxidising agent:—



According to Wallach methylhexanone is oxidised into  $\beta$ -methyladipic acid. But Markownikoff<sup>1)</sup> has recently stated, that when nitric acid is used as oxidising agent, only  $\alpha$ -methyladipic acid is obtained.

In order to discover whether methylhexanone is always attacked in the same manner, or whether the oxidising agent employed exerts some specific action, Bouveault and Tétray<sup>2)</sup> repeated Markownikoff's experiments; they found, however, that his statements were erroneous, and that, even when the oxidation is carried out with nitric acid,  $\beta$ -methylhexanone only yields  $\beta$ -methyladipic acid.

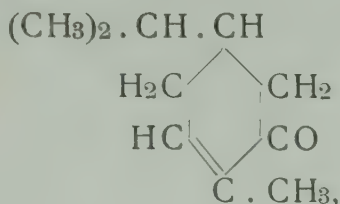
**Carvotanacetone.** It is well-known that thujone (tanacetone) when heated to  $280^{\circ}$ , is converted into a ketone  $\text{C}_{10}\text{H}_{16}\text{O}$  having a carvone-like odour, to which Semmler has given the name of carvotanacetone. A work by Harries<sup>3)</sup> deals with the relation of carvotanacetone to  $\Delta^6$ -menthene-2-on, a ketone which is formed from carvone hydrobromide by substitution of the atom of bromine by

<sup>1)</sup> Berliner Berichte 33 (1900), 1908.

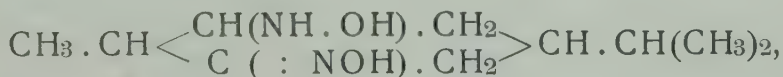
<sup>2)</sup> Bull. Soc. chim. III. 25 (1901), 441.

<sup>3)</sup> Berliner Berichte 34 (1901), 1924.

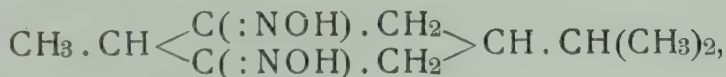
hydrogen. According to the author carvotanacetone is the racemic form, contaminated with other ketones, of the ketone



whose optically active modification is the dihydrocarvone or  $\Delta^6$ -menthene-2-on which is produced by gentle reduction of carvone hydrobromide. If carvone hydrobromide, dissolved in methyl alcohol, is reduced with zinc dust at a low temperature, part of the bromine product is reconverted into carvone, but the bulk passes over into the  $\Delta^6$ -menthene-2-on, a bright yellow strongly refractive oil, which boils at 227 to 228°, or under 9 mm. pressure at 96 to 97°, has a specific gravity of 0.9351 at 19°, and shows a dextrorotation of 49.5°. It has an odour like carvone, but somewhat fainter and sweeter. The semicarbazone which could readily be obtained, crystallises in tablets of regular form, and melts at 173 to 174°. The oxime forms oblique prisms of the melting point 75 to 77°. In addition to these, the ketone, when treated with an excess of hydroxylamine, yields an oxaminooxime melting at 95 to 97°:—



which in ethereal solution, when slowly oxidised by a current of air, is converted into the dioxime



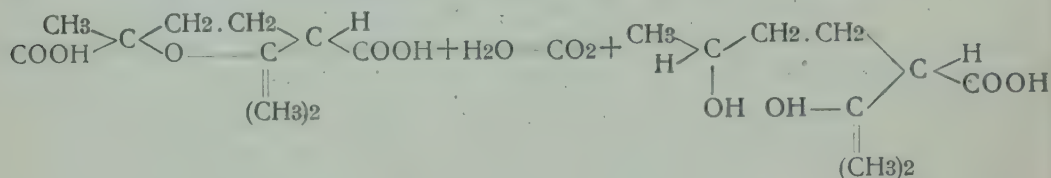
which crystallises in colourless prisms and melts at 194 to 196° with decomposition. Like carvone, this menthenone also yields a hydro-sulphide compound  $(\text{C}_{10}\text{H}_{16}\text{O})_2\text{H}_2\text{S}$ , which crystallises in brilliant needles of the melting point 222 to 225°, and which can be decomposed into its component parts by heating with alkali.

By reduction with zinc dust and sodium hydroxide in alcoholic solution, the ketone is converted into the well-known d-carvomenthone, and by treatment with aluminium amalgam into a syrupy dimolecular product, from which no crystallised diketone can be separated, but which yields with phenylhydrazine a phenylhydrazone, difficult to dissolve, and melting at 260°.

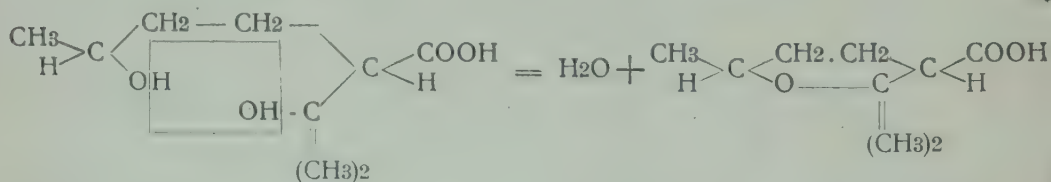
That the menthenone possesses the same carbon atomic skeleton as carvotanacetone; is proved by the fact that, like the latter, it is oxidised by permanganate solution into pyruvic acid and probably also into isopropyl succinic acid.

### Cineol.

In continuation of their earlier researches<sup>1)</sup> on the decomposition of cineolic acid, Rupe and Ronus<sup>2)</sup> have observed the formation of hexanol-2-methoethylol-5-acid-6 from cineolic acid, when the latter is heated in the autoclave with water to 160°:—



The acid crystallising from chloroform melts at 104.5 to 105°, dissolves very readily in cold and hot water, alcohol, and glacial acetic acid, but with difficulty in ether, benzene, ligroin and chloroform. When heated in a sealed tube to 150°, or distilled in vacuo, it is converted into cyclic cinenic acid:—



From this it might be concluded that the dioxyacid (hexanol-2-methoethylol-5-acid-6) is formed as the first product in the decomposition of cineolic acid, which then passes over into cinenic acid.

The authors further succeeded in isolating a liquid acid,  $\beta$ -cinenic acid, isomeric with cinenic acid. It boils at 124.5 to 125° (at 12 mm.) and represents an oily liquid, which dissolves with some difficulty in water. The  $\beta$ -acid can be converted, in the same manner as the cinenic acid first obtained ( $\alpha$ -acid), into the dioxyacid, for which both chemists have selected the name cinogenic acid, in consequence of its property, as an acid with open chain, of passing over into one belonging to the hydrocyclic series.

The new  $\beta$ -acid is also formed when  $\alpha$ -cinenic acid is heated under pressure with dilute sulphuric acid, and further from cineolic acid itself when heated with dilute sulphuric acid. This is the same

<sup>1)</sup> Berliner Berichte 33 (1900), 1136 and following; Report October 1900, 76. — Ibidem 33 (1900), 3541 and following; Report April 1901, 70 to 71.

<sup>2)</sup> Berliner Berichte 34 (1901), 2191 and following.

compound to which Rupe and Ronus already refer in their first communication, but its properties differ from those of the acid which Wallach and Gildemeister<sup>1)</sup> discovered in the dry distillation of cineolic acid. Specially characteristic is the calcium salt of  $\beta$ -cinenic acid, which separates out from an aqueous solution in small fascicular needles, with two molecules water of crystallisation. The calcium salt of the  $\alpha$ -acid is much more difficult to dissolve in water, and does not crystallise.

### Aldehydes.

Citral. An interesting essay by H. Hildebrandt<sup>2)</sup> deals with the fate of citral in the animal organism. The author administered citral to rabbits; and, as citral is readily converted by acids into cymene, he expected that in the urine of the animals either cumic acid itself would appear, or else a joined acid, which could be split up by mineral acid with formation of cumic acid. But the fate of citral is quite different; it is, on the contrary, oxidised in the animal body into a crystallising dibasic acid  $C_{10}H_{14}O_4$  of the melting point  $187^\circ$ , which can be separated from the urine by the addition of subacetate of lead. The same acid is obtained, when, instead of citral, geraniol is administered; the oxidation of geraniol in the animal body therefore occurs in this manner, that first of all the alcohol group  $CH_2OH$  is converted into the aldehyde group, and the citral thus formed is then further oxidised. Citronellol and citronellal, however, yield no analogous compounds.

But only a small portion — about 10 per cent — of the citral administered is converted into the dibasic acid. Subsequent tests have shown that it is exclusively the modification "a" of citral, which the animal organism is capable of digesting in the manner described.

Recently, however, the author found that in addition to the crystallised acid  $C_{10}H_{14}O_4$ , an oily acid of the same composition appears, which is present in the mother liquor of the former. Digestion with 60 to 70 per cent sulphuric acid converts the oily acid into a cyclic dibasic acid of the melting point  $96^\circ$ . Citral is consequently oxidised in the animal body into two isomeric acids  $C_{10}H_{14}O_4$ , one crystalline, the other oily. As geranic acid, in passing through the animal body, likewise yields these two acids, they may also be considered as oxidation products of the monobasic geranic acid. It may therefore be accepted that citral, in so far as it is not secreted joined to glucuronic acid, in the first place oxidises into monobasic geranic

<sup>1)</sup> Liebigs Annalen 246 (1888), 274.

<sup>2)</sup> Archiv für experimentelle Pathol. u. Pharmacol. Vol. 45 (1900), 121, and Chemisches Centralblatt 1901, II. 597.

acid, and that the latter is then converted into the two isomeric dibasic acids.

A notable difference has been found in the behaviour of the cyclic citral compounds as compared with those of purely aliphatic nature. Whilst the cyclic geranic acids are consumed in the animal body, leaving only traces of unchanged substances, the aliphatic geranic acid is oxidised into the dibasic acid  $C_{10}H_{14}O_4$ . This property of readily oxidising is also the cause why cyclo-citral,  $\alpha$ - and  $\beta$ -cyclo-geranic acids act with less energy on the organism than the corresponding compounds with open carbon chain.

**Citronellal.** The dimethylacetal of citronellal which Harries recently prepared and described<sup>1)</sup>, yields on oxidation with potassium permanganate, acetone and the dimethyl acetal of an aldehydo-acid which on saponification, as was shown by Harries and Schauwecker<sup>2)</sup>, yields the semialdehyde of  $\beta$ -methyladipic acid. The dimethylacetal of  $\beta$ -methyladipic acid is a liquid of a faint yellow colour, which on standing becomes dark red, and which possesses a somewhat acid-like odour. When kept for some time (or more rapidly when a small quantity of hydrochloric acid is added to the aqueous solution of the acetal) it is converted into 3-methyl-hexanal-1-carboxylic acid-6,  $OHC \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , — a colourless, strongly refractive, thick liquid with a pleasant odour. This semialdehyde of  $\beta$ -methyladipic acid shows properties both of an aldehyde and of an acid which was proved on the one hand by the formation of a semicarbazone melting at 156 to 157°, and on the other by the formation of the silver salt.

### Alcohols.

**Terpineol.** A new method of preparing terpineol has been mentioned by Genvresse<sup>3)</sup> who was led to it by his experiments on the action of nitrous acid on terpenes, such as pinene and limonene. Genvresse does not follow the earlier directions for the production of pinenol and limonenol. In order to produce terpineol, he prepares first of all an aqueous solution of nitrous acid, free from nitric acid; this solution, mixed with alcohol, he allows to act on the hydrocarbon, first at low and subsequently at ordinary temperature. After standing for eight days, during which time the solution is frequently shaken up, about one tenth of the pinene has been converted into terpineol; after two months this proportion has grown to about two-thirds of the pinene. It is then subjected to steam

<sup>1)</sup> Report October 1900, p. 78.

<sup>2)</sup> Berliner Berichte 34 (1901), 1498.

<sup>3)</sup> Compt. rend. 132 (1901), 637.

distillation, and the terpineol purified by fractionating in vacuo. The fraction passing over, under 15 mm pressure, between 110 and 125°, is treated with concentrated solution of sodium salicylate, the terpineol dissolved in it is separated, and purified once more by rectification. Upon the introduction of a small crystal of solid terpineol, the pure product solidifies completely, and it shows all the constants which Wallach has given for optically active terpineol. Terpineol can be produced either from d- or from l-pinene; in the first case dextrogyrate terpineol is obtained, in the second case one which is lævogyrate. For the production on a large scale this process seems hardly suitable.

**Myrcenol.** By hydrating myrcene, Power and Kleber obtained an alcohol  $C_{10}H_{18}O$ , which they considered as identical with linalool. Barbier<sup>1)</sup> doubts whether this supposition is correct, and he has therefore prepared a fairly large quantity of the alcohol from myrcene, which he calls myrcenol, and examined it more in detail. According to him it is an oily, colourless, strong smelling liquid, which slowly polymerises and thereby becomes fairly viscid. It boils under 10 mm pressure at 99 to 101°; at 14.5° it has the specific gravity 0.9012, and the index of refraction  $n_D = 1.47787$ . The acetate, formed from the alcohol by treatment with acetic anhydride, is colourless and possesses a very pleasant odour; it boils under the same pressure about 10 to 11° higher than the alcohol.

According to its origin myrcenol must be a tertiary alcohol. Its molecular refraction proves that it possesses two double linkages, whilst its physical constants show that it cannot be identical with linalool. Its constitution may be deduced from the products formed during the oxidation; if chromic acid mixture is used, it yields acetone, an aldehyde  $C_{10}H_{16}O$  which is not identical with citral (contrary to what is the case with citral, it can be regenerated from its oxime by boiling with a solution of oxalic acid, and then boils under 10 mm. pressure at 110°; its semicarbazone has the melting point 195 to 196°) — and lævulic acid; if the alcohol is first hydroxylised with permanganate solution, and then oxidised with chromic acid mixture, there is formed, besides a small quantity of acetone, only a mixture of lævulinic and succinic acids.

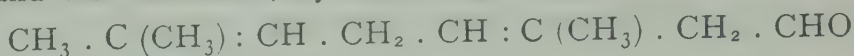
From the foregoing Barbier concludes that the same constitutional formula applies to myrcenol as that which had hitherto been given to linalool; myrcene would then have the formula:—



and the formation of the aldehyde  $C_{10}H_{16}O$  from the tertiary myrcenol might be thus explained, that, under the influence of the

<sup>1)</sup> Compt. rend. 132, 1048; Bull. Soc. chim. III. 25 (1901), 687.

sulphuric acid contained in the chromic acid mixture, myrcene is formed first, and that the latter, by absorbing oxygen, yields an aldehyde



isomeric with citral.

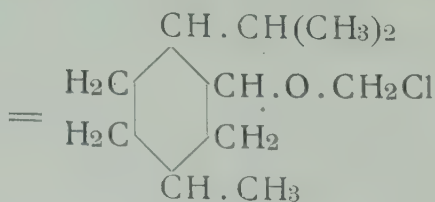
The author intends to return in a later communication to the question of the constitution of linalool, which must differ from that of myrcenol.

**Menthyl.** It is a well-known fact that menthyl chloride, formed by the action of phosphorus pentachloride on menthol, is not a uniform body, but a mixture of at least two isomers. N. Kursanow<sup>1)</sup> has contributed to the knowledge of this substance. He found that the optical activity of the chloride varies according to the length of time during which the phosphorus pentachloride has acted on the alcohol. If menthyl chloride is boiled with aniline, there remains a chloride with a fairly strong lævorotatory power ( $[\alpha]_D = -50^\circ 56'$ ), — a fact also observed by Slawinski with regard to the action of boiling alcoholic potash solution. If this chloride is boiled with sodium, it yields an optically active crystallising dimethyl  $\text{C}_{20}\text{H}_{38}$  of the melting point  $105.5$  to  $106^\circ$ , which is also obtained, along with a liquid isomer (also optically active) and small quantities of menthene and menthane, when menthyl chloride is treated in the same manner.

The stable menthyl chloride is, in the opinion of the author, a secondary chloride, for the tertiary halogen derivatives of menthol yield no dimethyl when treated with sodium. The liquid dimethyl formed from crude menthyl chloride is clearly an isomer of the crystallised dimethyl.

For further identification of the menthyl chloride which is not acted upon by alcoholic potash solution, Kursanow converted it with zinc ethyl into ethyl menthane  $\text{C}_{10}\text{H}_{19} \cdot \text{C}_2\text{H}_5$ , which, in the pure state, boils at  $207$  to  $208^\circ$  under  $736$  mm pressure, and which, like the material from which it was formed, is optically active.

If formaldehyde acts upon menthol under the influence of hydrochloric acid gas, it results, according to Wedekind<sup>2)</sup>, a chlormethyl menthyl ether  $\text{C}_{10}\text{H}_{19} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{Cl}$ .



<sup>1)</sup> Chemisches Centralblatt 1901, II, 346.

<sup>2)</sup> Berliner Berichte 34 (1901), 813.

an oil fuming in contact with air, which by the action of water is slowly split up into its component parts. When distilled under ordinary pressure it is also decomposed. The ether boils at 160 to 162° (16 mm.) and is lævogyre. Specific gravity = 0.9821.  $[\alpha]_D^{21} = -172.57^\circ$ .

A solution of the ether in xylene, when heated with sodium  $\beta$ -naphthol, yields methylene menthyl- $\beta$ -naphthyl ether



A second product formed by the action of formaldehyde on menthol is dimethylmethyal,  $C_{10}H_{19}O \cdot CH_2 \cdot O \cdot C_{10}H_{19}$ , whose formation had already been observed earlier by Brochet<sup>1)</sup> when formaldehyde reacted on menthol in the presence of sulphuric acid. Brochet calls the reaction product dimenthol formal. It melts at 56.5 to 57°, and distils, at 13 mm., above 220°. The body crystallises from alcohol in fine, small, felt-like needles.

### Quinones.

The presence of quinones as such in essential oils had hitherto not yet been observed. Hydrogenated quinones, on the other hand (that is to say in the form of ether), have been known for some time as constituents of essential oils; Oswald, for example, has detected hydroquinone (curiously in the form of its ethyl ether) in star-anise oil, whilst Sigel has found the dimethyl ether of thymohydroquinone in the oil of arnica root.

It is a matter of special interest that a quinone has now also been discovered in an essential oil. According to a communication from Brandel and Kremers<sup>2)</sup> the oil of *Monarda fistulosa* (wild bergamot) contains both thymoquinone and its hydrogenated product, thymohydroquinone of the melting point 140°. The simultaneous occurrence of these two compounds induces the authors to state, that in their opinion the oil of wild bergamot owes its colour to these two constituents, which have probably combined in the oil into the strongly coloured quinhydrone. Whether this surmise is correct, and especially whether it applies as a general rule, so that similar compounds may be assumed to exist in other dark-coloured oils, is a matter which must be cleared up by further examinations.

In a further work<sup>3)</sup> to which we would here refer, Brandel and Kremers report on the monoxime of thymoquinone ( $\Delta^{1,4}$ -terpadiene-3-oxime-6-on), the so-called nitrosothymol.

<sup>1)</sup> Compt. rend. 128 (1899), 612. — Bull. Soc. chim. III. 21 (1899), 370.

<sup>2)</sup> Pharm. Review 19 (1901), 200 and 244.

<sup>3)</sup> Pharm. Archives 4 (1901), 107.

**Aubépine** (Anisic aldehyde). There has been an exceptionally brisk demand for this body, which is used successfully for various modern perfume mixtures. In our opinion it is worthy of a thorough study in compositions with other synthetic perfumes.

**Benzyl acetate.** A strong demand from the South of France has suddenly developed for this preparation, which, as is well known, forms a constituent of natural oil of jasmine. There seems to be a possibility that similar bodies for strengthening natural perfumes will be in greater demand in the near future, when the want of extra-concentrated perfumes for export to countries wherein the import duties have been raised is felt more strongly. We are laid out for the manufacture of this product on a large scale, and are in a position to supply it in quantities at short notice.

**Citral.** The high prices of lemongrass oil have caused a considerable increase in the cost of manufacture. This article suffers moreover from the competition of less pure, and therefore less valuable, preparations, of which the disadvantages generally assert themselves in a disagreeable manner only when the working-up stage has been reached. Careful attention should therefore be paid to the characteristic properties of a pure product, and the presence of these explicitly insisted upon.

**Coumarin.** The great decline in the prices of carbolic acid has had a further effect on the value of this preparation, and has brought forward fresh competitors, anxious to take part in the contest for the ruin of this article. Years ago we have had careful trials made with regard to the solubility of coumarin in alcohol and water, and have published the result at the time. It seems necessary to bring the results, as given in the following table, once more to the notice of the consumers:—

100 parts alcohol:	dissolve:		
	at 0° C.	at 16—17° C.	at 29—30° C.
of 90 per cent by volume	7.1 parts	13.7 parts	42.5 parts
" 80 " " " "	6.0 "	12.3 "	38.3 "
" 70 " " " "	4.4 "	9.1 "	26.0 "
" 60 " " " "	3.2 "	6.0 "	16.0 "
" 50 " " " "	1.7 "	3.4 "	8.9 "
" 40 " " " "	0.7 "	1.5 "	3.9 "
" 30 " " " "	0.3 "	0.6 "	1.7 "
" 20 " " " "	0.2 "	0.4 "	0.8 "
" 10 " " " "	0.15 "	0.25 "	0.5 "
100 parts water	0.12 "	0.18 "	0.27 "

In order to prevent all precipitation of coumarin from the solution with a possible fall in the temperature, it is advisable not to use the entire maximum quantity given in the above table. If the quantity of coumarin soluble at 0° C. is taken as normal, it is certain that there is no possibility of a precipitate under ordinary circumstances.

Instead of the infusion of tonka beans, the spirituous solution of coumarin should now be used. If the infusion was prepared from

250 grammes tonka beans and  
1 kilo alcohol,

such infusion is completely replaced by the simple solution of

4 grammes coumarin in  
1 kilo 90 per cent alcohol.

The coumarin-content of best quality tonka beans has been taken as 1½ per cent.

**Eucalyptol, pur. cryst.** The preparation of the pure product, first manufactured by us, has been specially taken into consideration in planning our new Works. As soon as the manufacture is in full working order, we hope to be able to reduce the price so much, that the consumption will turn more and more from the ordinary eucalyptus oil to eucalyptol.

Such changes are not without example, as for instance in the case of anise oil and anethol, caraway oil and carvol, &c. There can be no question that the use of pure bodies in the place of many essential oils is bound to increase steadily.

**Eugenol.** This product has attained a certain importance since it was included in the 4<sup>th</sup> edition of the German Pharmacopœia. We supply it in an exceptionally fine, light-coloured quality, strictly in accordance with the official requirements.

**Geraniol from Citronella Oil.** (German Patent No. 76435.) Since the completion of our new factories, the manufacture of this product has now entered upon another stage, and we hope in a short time to be at last able to keep it in stock. In view of the difficulties met with in the supply of palmarosa oil, geraniol will be called upon to play a more important part than hitherto, and we hope that the possibility of obtaining it now in sufficient quantities, will stimulate new trials. Pure geraniol, such as supplied by us, is a magnificent body with an intense and pure rose odour.

**Geranyl Acetate.** (German Patent No. 80711.) Of the various esters of geraniol, geranyl acetate is the one which is most largely employed in perfumery and has been found the most useful in different compositions. At the same time, it is not possible to give

definite directions for its use; but the fact that it is purchased in pound lots, and that repeated orders are common, may perhaps be an inducement to give it a trial.

**Heliotropin** (Piperonal). Competition, as we feared, has caused a further decline in the prices, and this product which at one time was valued so highly, will now soon be quoted at such a low level that many makers will be induced to give up the manufacture. In our position as makers of safrol, which serves now exclusively as the raw material for this preparation, we can take a calm view of the further development of the quotations.

It is a subject of great interest to look back upon the previous quotations of this preparation, — a matter, for which the fact that it has now been on the market for about 25 years, may offer an excuse. In 1878 it was sold at 3000 Marks per kilo, from which price it gradually declined to 24 Marks. In 1885, long before the process was published, we took up the manufacture from safrol, and the competition increased gradually to such an extent that the value was brought down further and further, until it has reached its present level.

Heliotropin has become an article of extreme value for the perfumery, and it may be called, without fear of contradiction, one of the most important aromatic substances at the disposal of the perfumery industry.

**Linalool.** As already mentioned by us under the heading linaloe oil, pure linalool (first introduced to the trade by us in 1892) finds more and more favour for perfumery purposes, for it has been proved that all compositions in which it plays the leading part, — as for example “Lily of the valley”, are distinctly finer when linalool has been used in their preparation, than when they are made with linaloe oil. It is now taken for established beyond doubt that the alcohol linalool is the characteristic principal constituent of the oil.

**Menthol.** The exceptionally hot summer in Europe and America has exerted a powerful influence on the consumption of this prominent refreshing medium, and has also brought the useful migraine pencils back into favour.

Menthol is nowadays used for such a variety of purposes, that it has long since lost the character of an article of fashion, and has entered the ranks of indispensable medicaments. The preparations and specialities for which it is employed are legion.

In consequence of the brisk demand the prices have not only been maintained since the spring, but have gradually advanced by about 30 per cent. Moreover, the stocks in Japan are low, and the shipments have moved in such narrow limits, that there has been no chance of accumulating stocks either in Europe or America.

Export of crude menthol from Japan,  
from 1<sup>st</sup> January to 31<sup>st</sup> July 1901.

To Hong Kong . . . . .	5100 cattiees
„ India (Bombay, Singapore, &c.) .	2816 „
„ New York . . . . .	1875 „
„ London . . . . .	900 „
„ . . . . .	675 „
„ Hamburg . . . . .	357 „
„ Havre . . . . .	160 „
<hr/>	
Total	11,883 cattiees
<hr/>	
or about 16,200 lbs.	

Even if this year's harvest gives the hoped-for normal result, the prices will probably at least remain at their present level; but if there should be a deficiency, it is possible, in view of the strong demand, that the quotations will advance in a very pronounced manner. By opportune and important purchases of raw material (85 cases containing more than 2 tons are now on the way for us) we are in a position to supply the market liberally at current quotations.

**Safrol.** When reporting on camphor oil we already mentioned the changes which are imminent in the production of safrol. The Japanese Government is no longer willing to let us make the "large profits" which are said to have been made here, and it has erected at Kobe a safrol factory, which has been placed under the management of a Japanese chemist, Dr. Shimoyama, who has made his studies in Germany. It is stated that in this factory in future the so-called brown camphor oil (in which we discovered safrol in 1885) will be worked up into safrol, and placed direct upon the market. We have declined to take up the sale, as for several reasons we do not consider that this enterprise has sufficient vitality, and as, moreover, we have made arrangements which will enable us for many years to come, not only to continue carrying on the manufacture of safrol on the largest scale, but also to compete in every respect with the Japanese product.

This industry has already been carried on in Japan for several years by Americans, but does not seem to have prospered; as a matter of fact it has been limited to the production of an inferior product for the American market. The Japanese Government has now the intention of placing pure safrol on the market, and of monopolising the article. The future will show whether this project can be carried through. For the near future, and a good many years to come, this cannot be the case; for we have laid in such a stock of raw material, and carry on the manufacture in our new

Works with such special advantages, that it will be difficult to shake our position and to carry through the idea of a monopoly. It will only too soon become evident, that the world's consumption of safrol is not of sufficient importance, to base upon it a special industrial enterprise, at least not in a case like the present, where it is opposed by a well-introduced competitor working under the most favourable conditions.

**Terpineol.** The prices of this product vary as much as the qualities, and comparisons should only then be made, when it is a question of products of equal value. The constants and other properties of our make are accurately mentioned in our lists.

The results of our most recent investigations concerning terpineol, mentioned in our last Report, culminated, as is well-known, in the fact, that terpineol is not a uniform body, but, on the contrary, consists of a mixture of two terpineols melting at 35 and 32°.

When tested for their practical differences, and compared, they show no pronounced divergence in the odour, and are therefore so far only scientifically interesting.

**Thymol.** The important demand for this article, caused by its prolonged complete absence, has in a short time led to a hardening of the depressed prices. When higher quotations for ajowan seed came quite unexpectedly from India in August last, the market became very firm, and the advanced prices were readily paid for thymol. Exceptionally favourable transactions enable us to supply this preparation in large quantities at very advantageous rates, and at short notice.

We would here refer briefly to a process for preparing thymol chemically, which has recently been patented in France, and, if we are not mistaken, also in England. The crude material employed is 2-bromo-p-cymene-3-, or 5-sulphonic acid, which is debrominated and fused with potash. No experience of the yield of thymol by this process is at our disposal, but if we take into consideration the price of the crude material and the many transformations to which it has to be submitted, we cannot help thinking that thymol produced in this manner will be unable to compete in price with the natural product.

**Thymene.** We have again large stocks of this article, obtained as a by-product in the manufacture of thymol, which we can recommend as a substitute for oil of thyme in perfume mixtures for soaps. Thymene is exceptionally rich; to soap for domestic purposes it imparts a pleasant, refreshing odour, and there is probably no essential oil which covers the tallow odour in soaps better, or in a more lasting manner, than thymene.

**Vanillin.** Enormous competition has brought the price of this product to a level which nobody would have considered possible.

For the price of one kilo of the finest vanilla, one can now obtain the same quantity of the 50 times stronger vanillin — a fact which calls for admiration. In this connection the question rises involuntarily, what the present value of vanilla would be without the competition of vanillin? Whether it is to the interest of the consumer to take the price as the only criterion, is a question which for this preparation we would decidedly answer in the negative, and we would point to the many possibilities of adulteration which have already made themselves felt in previous years. Benzoic acid and acetanilide have been special favourites for this purpose. (See our Reports of October 1894, p. 79 and October 1898, p. 64.)

**Schimmel & Co.**



SEMI-ANNUAL REPORT

OF

SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ

NEAR LEIPZIG

LONDON & NEW YORK.

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APRIL 1902.

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## List of abbreviations.

$d$  = specific gravity at  $15^{\circ}$ , unless otherwise stated.

$d_{20}^{\circ}$  = specific gravity at  $20^{\circ}$ .

$d \frac{20^{\circ}}{4}$  = specific gravity at  $15^{\circ}$ , compared with water at  $4^{\circ}$ .

$\alpha_D 15^{\circ}$  = optical rotation, at  $15^{\circ}$ , in a 100 mm tube.

$[\alpha]_D$  = specific rotation.

$n_D 15^{\circ}$  = index of refraction at  $15^{\circ}$ .

$n$  = normal.

$\frac{n}{2} \left( \frac{n}{10} \right)$  = semi-normal or deci-normal (titrated solutions).

$g$  = gramme;  $cc$  = cubic centimeter;  $mm$  = millimeter.

Temperatures are uniformly stated in **centigrade** degrees ( $^{\circ}$ ).

At the time when we wrote the introduction to our last Report, of October 1901, we were under the influence of a depression felt throughout the German Industry, which has affected the entire economic and industrial life of the country.

The German Chemical Industry belongs to those sources of production which have, comparatively speaking, been least affected by the crisis, but nevertheless it has also suffered from its effects. Although the turnover on the whole may not have declined in any marked degree, there can be no doubt that here also in several branches an over-exertion has taken place, which in due course was bound to lead to over-production, and to depreciation of the values of raw materials and manufactured products. The falling-off in profits thereby caused is all the more acutely felt, as the brilliant results of the previous years were still fresh in everyone's memory. The disappointments which the year gone by has brought in many cases, will, it is hoped, give rise to reflections, whether the now flourishing system of cutting prices, and the tendency to manufacture anything without previously considering whether there is a sufficient demand for it, may not after all lead to dangerous side-paths.

On the whole the present crisis offers a somewhat brighter picture than former periods of decline, as the easy state of the money market, which, thanks to the excellent measures taken by the Imperial Bank, has now prevailed for a considerable time, greatly facilitates a return to normal conditions. In experienced circles the hope is entertained, that an all-round improvement of the entire economic situation in Germany is at hand, provided always that the commercial and tariff questions which are still in abeyance, may soon find a satisfactory solution, ending in long-continued commercial treaties.

In Germany the sale of our products was normal. In Austria-Hungary rumours of a spirit-monopoly are again in circulation, which, it is hoped, will not assume a concrete form.

The demand from the United Kingdom, France, Italy, Spain and Russia was normal; that from the United States may even be called very brisk and satisfactory.

On the other hand, the situation in almost all South American States is most unsatisfactory, particularly in Brazil, where the fluctuations in the exchange have grown to such dimensions, that every commercial calculation has become illusory, and that it is practically impossible to form an opinion on the conditions of credit. If to this be added the vexatious aggravation caused to the trade with Brazil by the notorious regulations respecting the making out and legalising of invoices, one can only feel pity for those who are dependent upon the trade with that country. In Colombia and Venezuela the situation is almost worse still, and these fields will have to be left out of account for German products for a considerable time. In the Argentine and Chile the political situation is not yet sufficiently clear to lead to a revival of trade and, with it, to a better state of credit.

In the Far East the situation is visibly improving. Japan, for example, again showed a regular demand. The export of our products to the Dutch Indies, Australia and the Philippines was also brisk, — to the last-named archipelago on account of the imminent increase in the import duties.

In the United States of America a strong movement has recently sprung up against the adulteration of essential oils, a practice which, according to observations made in that country, is constantly increasing. The 'National Wholesale Druggists' Association', a powerful union comprising all the good elements of the drug trade, which extends throughout the States, has provided in its organisation a special 'Committee of Adulterations', whose duty it is to counteract energetically the adulterations in the drug trade. This committee, at its last meetings in October last year, has exhaustively discussed the question of the adulteration of essential oils, and proved by means of voluminous reports, that the sale of inferior products is constantly on the increase in the drug trade. It is particularly emphasised that essential oils are almost universally bought under the description 'commercial', which is only a paraphrase of the word 'adulterated', and a strong recommendation is made to break with this system, and to discontinue the trade in such inferior products.

In Europe the situation is practically the same. A large proportion of the buyers only look to low prices, without considering that essential oils are articles of confidence in the truest sense, with which economy carried too far is out of place. We are engaged in systematically opposing this mischief by giving full information to the consumers, and our Reports serve this purpose in the first instance. Since their publication, or, rather, since the scientific study of essential

oils has been taken up in earnest, the trade in essential oils has received a moral support by which it has succeeded in gradually attaining the respected position which it now occupies, and which it will know how to maintain.

The changes affecting our branch, which have been inserted in the project of the new Tariff, have been discussed in detail in our last Report. This important question, as is well-known, is for the present still undecided.

During the past winter, research work has been diligently carried on in the interesting domain of essential oils and bodies pertaining thereto, of which the following pages again contain a fairly rich harvest.

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**Almond Oil, pressed from apricot kernels.** In the course of business the price of apricot kernels in Damascus has been further depressed by the abundant supplies, and this has found expression in a reduction of the quotations of the pressed oil. In January, deliveries to the ports of shipment were cut off for weeks by heavy falls of snow in the Lebanon mountains, a fact which threatened serious consequences for the production here, in view of the strong demand caused by the low prices of oil. Fortunately the interruption was only of short duration.

At the present value there can be no objection to laying in an ample supply, especially if the report is confirmed, received shortly before going to press, that the blossoms have been destroyed by gales.

The prices of essential oil of bitter almonds could also be reduced a little further.

**Almond Oil, pressed from sweet almonds, Ph. G. IV.** According to a communication from the United States consul at Malaga, the present year's crop of almonds in Europe and Morocco is estimated as follows:

	Tons		
	1899	1900	1901
Italy: Bari . . . . .	12 000	15 000	15 000
Sicily . . . . .	7 000	2 000	8 000
Spain . . . . .	5 000	2 000	4 000
Mallorca . . . . .	5 000	1 500	4 000
France (Provence) . . . . .	1 000	3 000	6 000
Portugal . . . . .	500	800	500
Morocco . . . . .	2 000	4 000	3 500
Totals	32 500	14 800	41 000

The prices have fallen considerably, in a degree corresponding to the larger yield. As early as December we were again in a position to fix reasonable quotations for almond oil.

Since the beginning of the year the quotations are again moving upwards, and to-day they are about 20 per cent higher than they were immediately after the harvest. An increase in the prices of oil is therefore imminent.

**Oil of Ambrette seeds.** This excellent oil, first distilled and introduced into commerce by our firm, has acquired a very satisfactory place in perfumery, and appears to be employed to advantage. The odour is exceptionally persistent and intense.

**Angelica Oil.** The stocks are decreasing rapidly, and may not suffice for the demand until the time of the new harvest. Large quantities are no longer obtainable.

**Anise Oil.** The prices of the oil distilled from Russian seed have gradually had to follow the higher quotations of the latter, and are now about 10 per cent higher than at the same time last year. It is a remarkable fact that it is all the more difficult to accommodate oneself to pay higher prices for ordinary oil, the more those prices approach those of anethol, whose dominating position becomes constantly more prominent, and for which new and important openings have been found in pharmacy since it has been included in the German (and, recently also in the Swedish) Pharmacopœia.

In spite of the condition of the Russian market, which justified a rise in the price, there were frequent opportunities of securing parcels of crude oil underhand at low rates from impecunious owners. We have at our disposal a splendid stock of crude material for anethol, bought at favourable prices, and will continue to give this speciality, as before, the greatest attention.

Recently there has been offered in the trade, at a higher price, an anethol which is said to be 25 per cent richer than the ordinary pure anethol. On closer examination, however, we proved that this product does not possess the quality claimed for it, but, on the contrary, shows a lower congealing point than our pure anethol. A greater richness is therefore out of the question. The results of other comparisons, made for the purpose of confirmation, were equally negative.

In Italy a liquid has recently also been placed on the market, by which, it is claimed, it is possible to intensify the flavour of anise. As the sale is carried on with the utmost secrecy, we suspect that we have here possibly to deal with a solution of saccharin. It is our intention to return to this subject after collecting exact details.

**Bay Oil.** This oil was first introduced by us into commerce in Europe in the year 1878, and recommended for application on the

American method. The beneficial, refreshing effect of the so called bay-rum as a hair-wash was here also readily appreciated, and led to the rapid adoption of this cosmetic. It affords us satisfaction to have taken the initiative in manufacturing such a favourite article.

For preparations of a low alcoholic strength we recommend the use of the extra-strong bay oil, of which 2 grammes are sufficient for producing 1 litre bay-rum. This quality oil should be used as fresh as possible, as the solubility decreases gradually.

**Cajeput Oil.** Transactions in this article are becoming less and less important, since the price of eucalyptus oil has fallen so much that the former can no longer be used for the production of cineol. Moreover, the direct importation in wine-bottles is a source of constant disappointments, as the size of the bottles has grown smaller and smaller, until now they hold only about 520 grammes net. Formerly they were of  $\frac{3}{4}$  litre size and held 600 grammes; now their size has diminished to  $\frac{6}{10}$  litre.

The importation in iron drums which, for that purpose, must be sent over specially, is not always feasible.

In the new edition of the Swedish Pharmacopœia, pure eucalyptol (cineol) has been substituted for cajeput oil.

The imports in Holland during the year 1901 came to about 6000 bottles. The stock at the close of the year was 1920 bottles.

**Calamus Oil.** The further examinations made by Thoms and Beckstroem<sup>1)</sup> have confirmed the fact that the so called calamus camphor  $C_{15}H_{26}O_2$  is an alcohol related to the sesquiterpenic alcohols, which on treatment with sodium forms a monosodium alcoholate. When boiled with 50 per cent sulphuric acid it passes over, with loss of two molecules water, into a hydrocarbon  $C_{15}H_{22}$ , for which the authors ascertained the following constants: boiling point at 15.5 mm pressure =  $144^\circ$ ; specific gravity at  $23^\circ = 0.9324$ ;  $(\alpha)_D^{26^\circ} = -11.31^\circ$ .

On treating a fraction of calamus oil, boiling at  $150-155^\circ$  under 10 mm pressure, with a 90 p. c. sol. of arsenic acid, Thoms and Beckstroem obtained a white plastic mass, from which with petroleum ether an oil could be abstracted, having the composition  $C_{15}H_{24}O$ , and a boiling point at 30 mm of  $180^\circ$ . This white mass is a compound of arsenic; on treating it with water, a body of the melting point  $173-184^\circ$  was obtained. Elementary analysis and determination of molecular weight proved that the product must be considered as a polymeride of asarone. As a check, the same body with the identical properties was formed from pure asarone submitted to the action of a 90 p. c. sol. of arsenic acid. The new product, to which the name

<sup>1)</sup> Apotheker-Zeitung 16 (1901), 688.

“parasarone” has been given, cannot be oxidised into asaric aldehyde. When distilled in vacuo it yields chiefly asarone.

The examination of the alcohols  $C_{15}H_{26}O_2$  and  $C_{15}H_{24}O$ , and of the hydrocarbon  $C_{15}H_{22}$ , and also of the mutual relationship of these bodies, is continued.

**Camphor Oil.** The removal of our factory from Leipzig to Miltitz has caused a prolonged interruption in the manufacture of the so called light camphor oil, and we were thereby prevented from supplying this article in large quantities. Since the work has been recommenced here on a large scale we are equal to the demand, and would ask our clients to bear our quotations in mind.

It is, of course, well-known, that the production of camphor in Formosa has been monopolised by the Japanese Government, and that the monopoly for this kind of camphor has been transferred to an English firm. But the production of camphor in Japan remained, as before, in the hands of private firms, and it was only natural that the value of the article could not always be kept at the level of the prices fixed by the monopolists, but, occasionally, moved backwards.

Under these conditions the Japanese Government was compelled to consider the question of also monopolising the camphor production of Japan. A bill to that effect has been brought before Parliament, but, as we are informed, has not been passed.

The Formosa Government will probably sooner or later take over the whole of the Japanese camphor, and work it jointly with the Formosa camphor, so that the production of both countries is under one single control. It remains to be seen whether the further exploitation in such case will also be granted to a private firm. Only when the whole world's production of camphor is controlled by one hand, it will be possible to keep up the value.

**Cananga Oil.** This product from the Dutch Indies has been manufactured on a scale greatly in excess of the demand, and large quantities of it are lying unsold at Batavia and the Dutch ports. The prices are correspondingly low. The over-production is the more to be regretted, and causes all the greater loss to the producers, as cananga oil readily becomes resinified, and is injuriously affected by prolonged storage. It is to be hoped that the present conditions will be a lesson to the Indian producers, and that the production will be considerably restricted, as otherwise this article also will soon go to ruin.

**Caraway Oil.** Holland supplied sufficient quantities of cheap material, whilst Scandinavia has not yet come forward with suitable offers. In the last-named country the opinions of the value are somewhat exaggerated, but, they will no doubt have to be modified in the end, as this year's seed for forward delivery can be bought

at lower figures in Holland. It is not to be admired that this article has also been made the subject of time-bargains, and that prices are already fixed while the caraway has scarcely been planted out.

The stocks still existing at this moment in Holland are estimated as follows:

1901 seed about	35 000	bales
older „ „	15 000	„
<hr/>		
Total	50 000	bales.

The cultivation which comes into account for this year's production of caraway is estimated:

in North Holland	at about	5 000	acres
„ Zeeland & Brabant	„ „	2 700	„
„ other provinces	„ „	1 000	„
<hr/>			
Total	about	8 700	acres.

Even under normal weather-conditions the crop will this year be smaller than in 1901, but the fairly important stocks will tend to keep the prices down, and on this expectation the present quotations for forward delivery are apparently based.

In the near future a decided change in the quotations of caraway oil and carvol (carvone) is not to be expected. We would avail ourselves of this opportunity to call attention to the low price of carvene, and to invite trials with this product, in the place of caraway oil, for the cheaper kinds of soap. Carvene is almost pure limonene. On closer examination of the odour the similarity with oil of sweet orange is distinctly noticeable. For this reason the usefulness of carvene as a perfume for soaps may be worthy of consideration.

**Cassia Oil (Chinese).** The value of this article has also gradually declined further during the last six months, and again approaches the low level of the notorious adulteration period of the year 1889, but with this difference, that the high-grade oils of 80—95 per cent aldehyde-content are now of irreproachable quality. As a matter of fact, adulteration now occurs only in exceedingly rare cases; as a rule, the oil is of good quality.

The present quotations in China are as follows:

60—65 per cent aldehyde	2/2	per lb.
65—70 „ „ „	2/3	„ „
70—75 „ „ „	2/4	„ „
75—80 „ „ „	2/6	„ „
80—85 „ „ „	2/8	„ „

A further reduction is considered impossible in China, an opinion with which we can only agree.

In consequence of a few suspicious observations recently made by us, we would recommend the Hong Kong export firms, when judging the oil, not to limit themselves exclusively to the determination of aldehyde, but also to make an examination of the residue in accordance with our directions, for it is not impossible that an oil of even 80 per cent aldehyde-content, may yet contain 10 per cent of solid resin or fatty oil, or both. The more the value of the article declines, the greater is the temptation for the Chinese to adulterate it again, and doubtless no one interested in the trade can desire a return to the old conditions, which we were only able to abolish after a fierce and prolonged struggle.

In the figures of the official statistics of the export from Hong Kong, the two articles cassia oil and star-anise oil are unfortunately grouped together, so that it is impossible to give the separate quantities of each.

The export of the two together, was:

	In the year 1901	6423 piculs
as against	" " " 1900	4201 "
	" " " 1899	3374 "
	" " " 1898	4461 "
	" " " 1897	4967 "
	" " " 1896	4177 "
	" " " 1895	2931 "
	" " " 1894	4439 "
	" " " 1893	4414 "

We estimate that of the above quantities about two thirds refer to cassia oil, which would give the export in the year 1901 as about 4300 piculs, or say 254 tons, having a value of nearly £ 100000. Hong Kong is at present the only port of shipment of this article.

**Cedarwood Oil.** In our Report of April 1901, page 59, we mentioned the distillate from the wood of the Atlas cedar, *Cedrus atlantica* Manetti. Of this oil, which had been produced for the first time, by way of a trial, at the Botanical Research Laboratory at Algiers, a first consignment of about 15 kilos has now arrived, and of this some 10 kilos are still for disposal. We shall soon be in a position to supply this oil regularly, as arrangements have been made for the distillation on a large scale. At the suggestion of Dr. Huertas, who has written a treatise on the subject, the manufacturer, Mr. Paul Boisse, pharmacien-lauréat, has given to this oil the name "Libanol Boisse", in order to avoid confusion with ordinary commercial cedarwood oil. This new name has been added to our lists. The maker has placed the sole rights of sale for Germany, Austria, the United Kingdom and the United States in our hands.



Citronella-grass plantation and distillation in Java.



With regard to the experiments made with this oil in the hospital at Mustapha, Dr. Trabut reports in the „Bulletin des Sciences pharmacologiques” of May 1900:

“Since 1880 I have constantly recommended the resinous products of the Atlas cedar in my publications, but only in 1898 one of my pupils asked my advice as to the direction of his studies concerning those constituents of this cedar which can be utilised for medicinal purposes. At my request Mr. Manquat received from the Department of Forestry the wood required for his preparations. The first distillation yielded an abundant quantity of coloured oil having a pleasant odour, which resembled the sandalwood oil of commerce. 12 litres of this oil were handed over to the pharmacy of the Civil hospital at Mustapha. My colleague, Professor Gemy, declared himself willing to make a trial with this new oil in the treatment of blennorrhœa. During the year 1899 more than 200 cases were treated with it, to the most complete satisfaction of my colleague, who stated that he preferred this cedarwood oil to sandalwood oil, and that it had the advantage of never causing pain in the kidneys. In short, the fatty wood of the fragrant and resinous Atlas cedar yields a balsamic product, which appears to be a suitable substitute for sandalwood oil. In order to avoid all confusion with other kinds of cedarwood oil, I propose to call it Atlas cedarwood oil.”

(The dose in blennorrhœa is 3 grammes daily, in capsules, during 6 to 8 days.)

Equally favourable is the report of Dr. H. Huertas who agrees that no secondary actions on the digestive organs and kidneys have been observed.

Favourable results have also been observed with Atlas cedarwood oil, as compared with sandalwood oil, in cases of bronchitis and tuberculosis. It is recommended in a mixture of 50 grammes with 950 grammes cod-liver oil, of which three spoonfuls are given daily. The Atlas cedarwood oil removes the disagreeable taste of cod-liver oil, and is on the whole readily taken by the patient, whose expectations rapidly diminish.

In cases of eczema it is applied in the form of an ointment of the following composition:

Atlas cedarwood oil 10 grammes  
Vaseline . . . . . 40 „  
To be applied twice daily.

If these favourable results are confirmed by experiments in European hospitals, the oil might be called to play an important part.

**Champaca Oil.** This oil, distilled by one of our friends, a chemist in the Philippines, from the fresh flowers of *Michelia Champaca* L., is considered a rarity, and has not been obtainable for years, in spite of a strong demand.

About two years ago it has at last again been possible to distil a limited quantity, of which we have about 600 grammes left in hand which is at the disposal of our clients.

As the oil cannot be obtained at regular intervals, it will be necessary for those who propose to push champaca products, to secure some of the oil at the earliest possible moment. We naturally endeavour to obtain regular supplies, but cannot guarantee a definite quantity.

**Cinnamon Oil, Ceylon.** In the course of the last few months the prices of fine Ceylon cinnamon chips have suffered a decline, which enabled us already in January to reduce our quotations of the well-known fine, sweet and heavy oil. They have never before been so low as at this moment.

Little was known up to now of the chemical composition of this valuable oil. In addition to cinnamic aldehyde as principal constituent, only eugenol and phellandrene had been detected with certainty. We have now made this oil the subject of a thorough examination, by which we have discovered in it a large number of interesting bodies. The most important points are mentioned in the following pages; a more detailed treatise will shortly appear in a scientific journal.

The material for the examination was supplied by 3,7 kilos of the highly volatile portions of 29 kilos of Ceylon cinnamon oil distilled by ourselves, which in the first instance were worked up in 9 crude fractions. The first two fractions were up to  $170^{\circ}$  re-fractionated at ordinary pressure, the others several times in vacuo.

Methyl-n-amyl ketone:  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ .

The first three fractions distilling from  $32$  to  $163^{\circ}$ , were treated with bisulphite, and from the crystalline double compound a ketone was isolated, which was recognised as methyl-n-amyl ketone. Its semicarbazone melts at  $122$  to  $123^{\circ}$ . Two combustions of this body gave figures corresponding to the formula  $\text{C}_8\text{H}_{17}\text{ON}_3$ :

1. 0,1438 g of the subst. yielded 0,1273 g  $\text{H}_2\text{O}$  and 0,2969 g  $\text{CO}_2$ .
- 2 0,1449 g " " " " 0,1298 g  $\text{H}_2\text{O}$  " 0,2988 g  $\text{CO}_2$ .

Calculated for  $\text{C}_8\text{H}_{17}\text{ON}_3$ :

Found:

C	56,14 per cent.	56,30 per cent.	56,24 per cent.
H	10,00 " "	9,83 " "	9,95 " "

The methyl-n-amyl ketone found in the first runnings of oil of cloves<sup>1)</sup> yields a semicarbazone of the same melting point. The methyl isoamyl ketone, prepared for comparison, yields a semicarbazone of the melting point  $142$ — $143^{\circ}$ .

<sup>1)</sup> Report April 1897, 46.

Furfurol:  $C_4H_3O \cdot CHO$ .

The mixture of methyl amly ketone and benzaldehyd isolated from the first fractions distilled in the following three fractions:

1. 54—95°. 2. 95—165°. 3. 165—180°.

Of these No. 2 and 3 gave an intense furfurol reaction with a solution of aniline hydrochlorate in aniline.

Pinene:  $C_{10}H_{16}$ .

Fraction 160—165° had a pronounced terpene odour. Specific gravity 0,8695 at 15°; optical rotation,  $\alpha_D = -15^\circ 10'$ . The nitrosochloride of the melting point 102—103°, and the nitrol benzylamine melting at 122—123°, obtained from the former, proved the presence of pinene.

Phellandrene:  $C_{10}H_{16}$ .

Fraction 170—174° (42—43° at 4—5 mm pressure) had the specific gravity 0,8614 at 15°; the optical rotation  $\alpha_D$  was  $-5^\circ 4'$ .

The presence of phellandrene was proved by the nitrite, whose melting point 102°, after recrystallisation from acetic ether and cold methyl alcohol, rose to 103—104°. ( $\alpha_D$ ) =  $+11^\circ 39'$  in chloroform solution.

The analysis gave the following values:

0,1517 g of the subst. yielded 0,1019 g  $H_2O$  and 0,3154 g  $CO_2$ .

0,1445 g " " " " 17,4 cc N at 19°, at 750 mm pressure.

Calculated for  $C_{10}H_{16}N_2O_3$ :

Found:

C 56,60 per cent

56,70 per cent

H 7,55 " "

7,51 " "

N 13,21 " "

13,65 " "

A nitrite of the melting point 119—120°, which according to Schreiner<sup>1)</sup> (as we can confirm) is obtained from phellandrene of eucalyptus oil, could not be detected.

Cymene:  $C_{10}H_{14}$ .

For the identification of this body, a fraction boiling at 48°, at 4—5 mm pressure, was first oxidised in the cold with dilute permanganate solution, for the purpose of decomposing present terpenes, and the oil driven over with water vapour was boiled for some time with sodium in order to remove possible oxygenated bodies. The oil, thus purified, boiling at 175—177°, yielded on oxidation with 1 to 2 per cent permanganate solution, with the application of heat, an acid of the melting point 154—156°, p-oxyisopropyl benzoic acid, whose mother

<sup>1)</sup> Pharmaceutical Archives 4 (1901), 90.

liquors, heated with concentrated hydrochloric acid, yielded propenyl benzoic acid of the melting point  $161-162^{\circ}$ , which dissolves with difficulty in water. There was further obtained terephthalic acid, which also occurs in the oxidation of cymene.

**Benzaldehyde:**  $C_6H_5 \cdot CHO$ .

Some of the oil boiling at  $168-171^{\circ}$  ( $45^{\circ}$  at 4—5 mm pressure) was treated with bisulphite. The aldehyde regenerated from the bisulphite compound distilled at  $174-179^{\circ}$ , and was found to be heavier than water. The body was identified as benzaldehyde by the phenylhydrazone melting at  $156^{\circ}$ , and the semicarbazone of the melting point  $213-214^{\circ}$ .

**Nonylic aldehyde:**  $C_9H_{18}O$ .

In the fractions boiling above  $180^{\circ}$  ( $62-92^{\circ}$  at 6—7 mm pressure), nonylic aldehyde was detected, in addition to benzaldehyde, cinnamic aldehyde and the aldehydes mentioned below. This body, recently isolated by us from rose oil, was proved by the nonylic acid (peltargonic acid), obtained by oxidation of the aldehyde with moist silver oxide. Three analyses of its silver salt gave the following figures:

1. 0.3129 g of the substance left 0.1271 g Ag.

2. 0.3990 " " " " " 0.1613 " "

3. 0.2524 " " " " " 0.1040 " "

Calculated for

$C_9H_{17}O_2$  Ag:

Found

	1.	2.	3.
Ag 40.75 per cent	40.62 per cent;	40.53 per cent;	41.20 per cent.

We were unable to obtain from the aldehyde mixture, for further identification of the aldehyde, the semicarbazone of the melting point  $89^{\circ}$  which had been produced by v. Soden and Rojahn<sup>1)</sup> from nonylic aldehyde. On the other hand, we received a semicarbazone melting at  $116-118^{\circ}$ , which may be considered with some degree of certainty as a derivative of hydrocinnamic aldehyde.

**Hydrocinnamic aldehyde:**  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CHO$ .

The semicarbazone melting at  $116-118^{\circ}$  gave the following values on analysis:

1. 0.1501 g of the subst. yielded 0.0956 g  $H_2O$  and 0.3438 g  $CO_2$ .

2. 0.1572 " " " " " 0.0954 " " " 0.3617 g "

Calculated for  $C_{10}H_{13}ON_3$ :

Found:

C 62.83 per cent

H 6.81 " "

1.

62.56 per cent

7.06 " "

2.

62.75 per cent

6.74 " "

<sup>1)</sup> Berliner Berichte **34** (1901), 2809.

Repeated re-crystallisation from hot ether raised the melting point to  $126^{\circ}$ . The semicarbazone prepared for comparison from synthetic hydrocinnamic aldehyde melted at  $130-131^{\circ}$ . Paucity of material rendered a definite proof of the identity of the two products impossible. The semicarbazone of the melting point  $126^{\circ}$ , heated with dilute sulphuric acid, gave the characteristic odour of hydrocinnamic aldehyde.

### Cumic aldehyde: $C_{10}H_{12}O$ .

From the bisulphite liquors from which the double compounds of the aldehydes mentioned above had separated as solid products, a small quantity of an aldehyde was obtained which had the odour of cumic aldehyde. Its semicarbazone melted at  $201-202^{\circ}$ , and yielded on combustion values corresponding to those calculated for the semicarbazone of cumic aldehyde.

1. 0.1481 g of the subst. yielded 0.1002 g  $H_2O$  and 0.3494 g  $CO_2$ .

2. 0.1475 " " " " " " 0.0991 " " " 0.3457 " "

Calculated for  $C_{11}H_{15}ON_3$ :

Found:

		1.	2.
C	64.39 per cent	64.35 per cent	63.93 per cent
H	7.32 " "	7.52 " "	7.47 " "

The semicarbazone obtained from cuminol had the same melting point; the mixture of the two products also melted at  $201-202^{\circ}$ . On oxidation of the aldehyde with moist silver oxide, cumic acid of the melting point  $114-116^{\circ}$  was obtained; a mixture of this acid with pure cumic acid melted at the same temperature.

### Linalol: $C_{10}H_{18}O$ .

The fractions of the boiling point  $80-92^{\circ}$  (at 6—7 mm pressure), freed from aldehydes by bisulphite solution, were rectified in vacuo, and the portions distilling at ordinary pressure at  $195-205^{\circ}$ , which had a distinct linalol-like odour, were oxidised in the cold with chromic acid mixture. The specific gravity of this fraction was 0.8772, the optical rotation  $-8^{\circ} 32'$ . The resulting aldehyde purified by the bisulphite compound had the odour of citral; when heated with pyruvic acid and  $\beta$ -naphthylamine, it yielded citryl- $\beta$ -naphthocinchonic acid of the melting point  $197^{\circ}$ .

### Linalyl isobutyrate: $C_{10}H_{17} \cdot OCOC_3H_7$ .

Linalyl isobutyrate appears also to be present. When saponifying the fractions boiling between 80 and  $111^{\circ}$  (at 6—7 mm pressure) and having been treated with bisulphite, which on the average gave the saponification number 20.4, there was isolated, in addition to an acid with a pungent odour (possibly formic acid), another acid with a

distinct odour like St. John's bread. The silver-content of its silver salt did not, however, agree with the value calculated for silver isobutyrate, which may have been caused by added silver formate or acetate.

Eugenol:  $C_{10}H_{12}O_2$ .

In order to detect eugenol, "heavy Ceylon cinnamon oil" was shaken with 2 to 3 per cent potash liquor; the oil separated from the alkaline solution by acid gave the blue eugenol reaction with ferric chloride, and yielded with benzoyl chloride and soda liquor, benzoyl eugenol of the melting point  $69-70^\circ$ .

A fraction of the boiling point  $97^\circ$  (at 5 mm pressure) from which the eugenol had been removed, gave a very distinct methoxyl reaction when examined in Zeisel's apparatus. Our supposition that eugenol methyl ether might possibly cause this reaction, was not confirmed; at least we did not succeed in obtaining by oxidation, either with chromic acid mixture or with permanganate of potassium, the readily identified veratric acid. Instead of this we only obtained greasy products.

Caryophyllene:  $C_{15}H_{24}$ .

This sesquiterpene could be detected in one of the last fractions, boiling at  $104^\circ$  (at 5 mm pressure).

The specific gravity of the portion distilling at  $260-261^\circ$  was 0.9047, the rotatory power  $\alpha_D = -7^\circ 20'$ .

Two analyses gave the following values:

1. 0.1904 g of the subst. yielded 0.2012 g  $H_2O$  and 0.6133 g  $CO_2$ .
2. 0.1240 " " " " " 0.1284 " " " 0.3984 " "

Calculated for  $C_{15}H_{24}$ :

Found:

		1.	2.
C	88.23 per cent	87.85 per cent	87.63 per cent
H	11.76 " "	11.74 " "	11.51 " "

For further identification caryophyllenic alcohol was produced from it, of which the melting point was found at  $95^\circ$ . Two combustions yielded values corresponding with those calculated for an alcohol  $C_{15}H_{26}O$ :

1. 0.2277 g of the subst. yielded 0.2366 g  $H_2O$  and 0.6727 g  $CO_2$ .
2. 0.1819 " " " " " 0.1923 " " " 0.5399 " "

Calculated for  $C_{15}H_{26}OH$ :

Found:

		1.	2.
C	81.08 per cent	80.57 per cent	80.95 per cent
H	11.71 " "	11.55 " "	11.75 " "

The phenyl urethane melted at 136—137°. This proves the presence of caryophyllene.

According to the foregoing, the following bodies have therefore been detected in Ceylon cinnamon oil:

- |                         |                                                 |
|-------------------------|-------------------------------------------------|
| 1. Cinnamic aldehyde    | } already previously detected,<br>partly by us. |
| 2. Phellandrene         |                                                 |
| 3. Eugenol              |                                                 |
| 4. Methyl-n-amyl ketone |                                                 |
| 5. Pinene               |                                                 |
| 6. Cymene               |                                                 |
| 7. Furfurol             |                                                 |
| 8. Benzaldehyde         |                                                 |
| 9. Nonylic aldehyde     |                                                 |
| 10. Cumic aldehyde      |                                                 |
| 11. Linalol             |                                                 |
| 12. Caryophyllene.      |                                                 |

It is also fairly certain that it contains:

13. Hydrocinnamic aldehyde, and
14. Linalyl isobutyrate.

**Citronella Oil (Ceylon).** The fluctuations, which the value of this important article has undergone during the last six months, are so trifling that they may be left out of account. The sensational reports, which regularly make their appearance at certain periods, that at the low quotations the distillation no longer pays, and is slowly becoming extinct, are refuted by the fact that the export again shows an increase, as compared with that of the previous year.

It amounted to

	1430168 lbs. in 1901
against	1409050 " " 1900
	1478756 " " 1899
	1365917 " " 1898
	1182867 " " 1897

The figures of the export of 1899 have up to now not been reached again.

There can be little doubt that with a selling price of about 2/- per kilo, the manufacture of citronella oil is not very remunerative, more particularly as the present state of the knowledge of the article renders the profitable adulteration of the oil, which used to be the order of the day, an extremely difficult matter. At the same time,

the unfair trading in this article has not yet been completely done away with, for samples are constantly being submitted for our opinion, which do not answer the conditions specified by us. In view of the unexampled cutting which prevails in citronella oil, the greatest care is required in purchasing.

We have obtained extraordinary results with the Java citronella oil specially distilled for us. This product shows clearly what can be obtained by rational, expert cultivation and distillation of the crude material, for the species of plant used in Java is the same as in Ceylon. And yet what a vast difference between these two oils!

It affords us great pleasure to be able to present to our readers on the next page a picture showing part of the plantation on which this oil is produced. In the foreground is seen a field planted with citronella grass. The building on the left contains the apparatus used for distilling the oil. In view of the interminable trouble and care caused by undertakings of this character in such far-off countries, it is sincerely hoped that the excellent product may constantly increase in favour, and may meet with the appreciation to which it is justly entitled, so that the manufacture may be continued on a large scale. If produced on a small scale, the expenses are proportionately too high.

We shall be pleased to supply samples.

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A long time ago already Dodge<sup>1)</sup> mentioned the supposition that, in addition to geraniol, another alcohol is present in citronella oil, which corresponds to the "reduction product of citronellal". Flatau and Labbé<sup>2)</sup> also stated briefly, on the strength of their method for separating geraniol and citronellol, that citronella oil contains 6 per cent of citronellol. But as this in no way definitely proved the presence of citronellol in citronella oil, we have ourselves made a thorough examination of the oil for this purpose. We did not succeed in detecting citronellol in Ceylon citronella oil; on the other hand, we were able to prove its presence in citronella oil from Java.

The crude geraniol fractionated from the Java oil was treated with calcium chloride, and the portion which did not react was washed out with petroleum ether. The oil obtained by evaporating the ether was distilled; for the purpose of decomposing the geraniol, an equal weight of phthalic acid anhydride was added, and the whole heated for about 12 hours on a water bath. The acid phthalic ester of citronellol thus formed was dissolved in the proportionate quantity

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<sup>1)</sup> Am. Chem. Journ. **11** (1889), 456.

<sup>2)</sup> Compt. rend. **126** (1898), 1726.

of dilute soda solution, and the decomposed geraniol removed by repeated shaking with ether. By saponification of the aqueous solution of ester salt with potash liquor, we obtained a citronellol which after fractional distillation possessed the following constants:

$$d_{15}^{\circ} = 0.866; \alpha_D = + 1^{\circ} 45'.$$

In order to remove the remaining quantity of geraniol, the product obtained was again purified in the manner mentioned above. The citronellol now resulting agreed in its physical constants (all excepting the rotation, which is  $+$ ) with those of l-citronellol from geranium oil. The following table gives full particulars on the subject:

### Citronellol.

	Boiling point	$d_{15}$	$\alpha_D$	$n_{D22^\circ}$	Melting point of the silver salt of the phthalic ester	
from Java citronella oil	$109^\circ$ (7 mm)	0.8619	$+ 2^\circ 32'$	1.45671	} 125—126°	
	$103^\circ$ (5 mm)	0.8604	$+ 2^\circ 13'$	1.45651		
	$103^\circ$ (5 mm)	0.8629	$+ 2^\circ 7'$	1.45791		
from geranium oil	225—226° (764 mm)	0.862	$- 1^\circ 40'$	1.45611 <sup>1)</sup>	125.5—126.5°	
	114—115°	0.856	$- 1^\circ 40'$	1.45609 <sup>2)</sup>		
	(12—13 mm) at 22°					

For purposes of identification the silver salt of the acid phthalic ester was used. The solution of sodium salt obtained by heating the citronellol for two hours with phthalic acid anhydride, and dissolving the melted mass in soda solution, was once more purified by shaking it with ether. In order to remove the sodium phthalate, the sodium salt of the ester was separated by common salt and then dissolved in water. The acid ester was next liberated with sulphuric acid, extracted by ether, the ethereal solution dried, and the ether distilled off. From the acid ester the silver salt<sup>3)</sup> was formed by means of the ammonia salt, and recrystallised from benzene and methylalcohol. The melting point was at 125—126 $^{\circ}$ . Erdmann found it at 120—124 $^{\circ}$ , and that of the silver salt of geranyl phthalic ester at 133 $^{\circ}$ . For comparison the silver salt of the ester of l-citronellol of geranium oil was prepared; this melted at 125.5—126.5 $^{\circ}$ .

<sup>1)</sup> Report, April 1898, 57.

<sup>2)</sup> Wallach, Nachr. d. Kgl. Ges. d. Wiss. zu Göttingen 1896, I. 64.

<sup>3)</sup> See Erdmann, Journ. f. pract. Chemie II. 56 (1897), 41.

The determination of silver gave the following results:

		Ag found	Ag calculated
1. Silver salt from citronella oil citronellol	Substance = 0.8088 g Ag = 0.2120 g	26.21 per cent	26.27 per cent
2. Silver salt from geranium oil citronellol	Substance = 0.3096 g Ag = 0.0814 g	26.29 per cent	

From this it would appear that now for the first time natural dextrogyre citronellol has been detected.

**Clove Oil.** According to the official reports from the German Consulate at Zanzibar, the clove harvest extends over the whole year, commencing in the beginning of July and lasting until the end of June. This report states further: from 1<sup>st</sup> July 1900 to 30<sup>th</sup> June 1901, 250000 frazileh have been brought to the market. An average crop was formerly estimated at 375000 frazileh, but should now, no doubt, be taken at a lower figure, as the trees have been neglected through lack of labour. The prospects of the 1901/1902 harvest are said to be good; it is hoped that the yield will be 400000 frazileh, or 14000000 lbs.

The export was:

	lbs.	Value in Rupees
in 1898 . . .	10856566	2155956
„ 1899 . . .	16593340	2958487
„ 1900 . . .	11788095	2372227

It was divided as follows:

	1898	1899	1900
	Quantities in lbs.		
Europe . . . . .	4138086	8028780	5235388
America . . . . .	729960	648970	719600
Asia . . . . .	5912800	7599517	5769293
Africa . . . . .	75720	316073	63814
	Value in Rupees		
Europe . . . . .	797375	1394217	1031952
America . . . . .	149402	110108	150079
Asia . . . . .	1194032	1397837	1177754
Africa . . . . .	15147	56425	12442

The export to America was exclusively to New York; that to Asia, to Bombay, of which perhaps part has been reshipped to Europe.

The export to the various European ports was made up as follows:

	1899	1900	1899	1900
	lbs		Rupees	
Rotterdam . . . . .	4473 240	2 674 160	786 212	537 810
London . . . . .	1 432 475	1 404 968	254 852	274 520
Hamburg . . . . .	1 249 850	715 260	204 267	122 912
Marseilles . . . . .	292 215	217 000	51 229	49 800

To Rotterdam's share should be added 84 000 lbs., value 18 000 Rupees, shipped to that port via Amsterdam.

Clove stems were exported:

	Quantities in lbs.			Value in Rupees.		
	1898	1899	1900	1898	1899	1900
To Europe .	584 640	3 605 245	1 743 426	24 055	104 351	70 453
„ Asia . . .	305 561	216 483	220 447	14 845	6 748	11 621
„ America .	336 875	555 940	98 000	19 657	31 708	7 700

Whilst in the previous year the export to America was more than double that to Asia, the former has now become quite unimportant. It is shipped to New York and Bombay. In Europe, Hamburg takes the first place:

	1898	1899	1900
	Quantities in lbs.		
Hamburg . . .	456 890	2 980 110	1 478 226
London . . . .	74 900	370 335	83 160
Marseilles . . .	38 850	179 900	28 000

But in clove stems also Rotterdam enters strongly into competition. The import amounted in 1900 already to 112 000 lbs., to which should still be added 42 000 lbs. from Amsterdam.

At the time of going to press, the official Annual Report from Hamburg for the year 1901 has, unfortunately, not yet appeared, and we regret that we shall this time miss its valuable opinion on the probable course of the prices of cloves. We know, however, from private sources, that the situation is considered with more composure there than on the Dutch market, where the view appears to be somewhat obscured through the influence of special interests in the terminal market.

The reports emanating from Holland are in some respects in direct contradiction to the official consular reports; in others their calculations, or rather estimates, anticipate events in such a phantastic manner, as to astonish every thoughtful reader. In the statistics of one

of these reports, dated January of this year, the estimates made include not only the yield of the harvest 1902 to 1903 (i. e. commencing in July 1902 and ending in June 1903), estimated at 3 000 000 kilos, but also the consumption from 1<sup>st</sup> September 1902 to 31<sup>st</sup> August 1903 (5 400 000 kilos) and even the stock in September/October 1903 (2 420 000 kilos)! And as the stocks on 1<sup>st</sup> January 1902, at all the principal markets, amounted in the aggregate to 137 000 bales or 8 220 000 kilos, the anticipated reduction of the stocks by September/October 1903, by 5 800 000 kilos, is used as an argument for an increase in the prices of cloves!

It is not necessary to comment upon these speculations. We would consider it extremely risky to conclude transactions in cloves on the strength of such views. In our opinion the present values are normal, and we believe that there is no risk whatever in now laying in a stock of oil of cloves.

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For the purpose of isolating the methyl-n-amyl ketone present in oil of cloves, we have again taken up our previous examinations. The portions of the first runnings of the oil, which boiled up to 159° were treated with bisulphite. On decomposing the solid bisulphite compound, an odour arises which strongly excites coughing, and which probably originates from valeraldehyde. The ketone freed from furfurol by oxidation with a 1—2 per cent solution of permanganate, distilled at 151—153°. The specific gravity at 0° was found to be 0.8332; at 15°, 0.8223. No optical rotation was shown. By means of its semicarbazone melting at 122—123° its identity with the ketone of Ceylon cinnamon oil<sup>1)</sup> was ascertained. When the fractions distilling at 200—240° were saponified, benzoic acid was isolated in considerable quantity. It was identified by the melting point (121°), the formation of a sublimate, and the occurrence of the odour like methyl ester of benzoic acid on heating with methyl alcohol and sulphuric acid. As methyl alcohol had already been detected in clove oil, it may be assumed that methyl ester of benzoic acid is a constituent of the oil. It was again impossible to detect terpenes in the corresponding fractions.

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In the Transactions of the German Chemical Society, A. Verley and Fr. Bölsing publish a new method for the quantitative determin-

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<sup>1)</sup> See under this heading.

ation of alcohols and phenols, with special reference to eugenol<sup>1)</sup>. This method proves a simplification of the acetylation method, as, after esterification by means of a known quantity of acetic anhydride, the acetic acid not combined with alcohol is titrated back, and the alcohol-content thus ascertained. It is based on the following: Whilst a mixture of alcohols (or phenols) with acetic anhydride reacts but slowly at a low temperature, a strong reaction occurs immediately, with a great increase in the temperature, if pyridine be present, whereby the acetic acid formed during the process at once combines with the pyridine and, for this reason, the ester formed cannot possibly be saponified again. Pyridine behaves in a neutral manner towards phenol-phthaleïn, and it is therefore an easy matter to determine, by titration, the quantity of acetic acid contained in a mixture with pyridine.

Verley and Bölsing proceed as follows: 1 to 2 grammes of the alcohol, or phenol, as the case may be, are placed in a flask of about 200 cc capacity, together with 25 cc of a mixture consisting of about 120 grammes acetic anhydride and 880 grammes pyridine, and heated on a water bath for 15 minutes. After cooling, the whole is diluted with an equal quantity of water, (for the purpose of converting the acetic anhydride, which is still unchanged, into acetic acid, or pyridine acetate), and the acetic acid not combined with alcohol (or phenol) is titrated back. As the content of acetic acid of the mixture mentioned above has also been ascertained by titration, the quantity of acetic acid combined with alcohol (or phenol) is readily determined, and from it the alcohol (or phenol)-content can be found.

In the work referred to, numerous tests are published, which partly show excellent results, and therefore tell greatly in favour of this method. In a few cases, however, Verley and Bölsing have arrived at negative results, for example in the determination of terpinol, geraniol, linalol, benzyl alcohol, and others.

As already stated, the authors enter more in detail into the determination of eugenol in oil of cloves, and in that case also endeavour to prove, by means of a series of analyses, the serviceableness and reliability of their method. They attack at the same time the methods introduced by Umney and Thoms, and place the results thereby obtained against those obtained by their method, a comparison which undoubtedly brings to the light some very important differences.

We have so far made but few determinations by the method proposed by Verley and Bölsing, and we are therefore not in a

<sup>1)</sup> Vol. 34 (1901), 3354.

position to form a conclusive opinion on the matter, but we shall not fail to return fully to the subject in our next Report.

**Cubeb Oil.** The importance of this article is diminishing, and the demand for it, in spite of the low price, is now considerably smaller than previously. The price of cubebs became more depressed since the failure of an attempt to raise the quotations, which was made during the summer. The owners of large parcels in Holland are holding back, but speculators have completely disappeared from the market. The sales in Holland during the year 1901 amounted only to 144 bales; the quantity remaining unsold was 556 bales.

**Cypress Oil.** This excellent remedy against whooping cough increases constantly in favour, but comparatively few chemists keep it in stock, a fact which is all the more to be regretted, as its use in the very earliest stages of the disease is especially important to ensure good results. In consequence of this we constantly receive applications for this oil from private individuals, whom we naturally again refer to known chemists.

**Essential Oils, Sicilian and Calabrian.** As in previous years, we have once more pleasure in giving an annual statistical review of the export of essential oils from Italy during the year 1901, for which we are again indebted to the courtesy of Mr. Eduardo Jacob, the German Consul at Messina.

It appears from these figures, that the export during 1901 has fallen behind that of the previous year by 21624 kilos, whilst the value shows an increase of 1342435 Lire. This is explained by the high prices of essential oils during the first ten months of 1901, which on the one hand appear to have led to a slight decrease in the consumption, but on the other hand have caused a not inconsiderable increase in the value of this smaller export.

Nevertheless it is a remarkable fact that, in spite of the higher prices, the export to foreign countries has been so important, and, with the only exception of the year 1900, has even far exceeded the figures of any of the last ten years. This may be taken as a proof that the demand from abroad grows from year to year, and lays constantly increasing claims to the market — from which the moral may be drawn, that the consuming public should take the fullest possible advantage of favourable opportunities, when prices rule low, as in future even a slight falling-off in the harvest may again lead to higher prices.

Such a state of affairs has arisen during the last four months; it must be attributed chiefly to the fact that the crop of fruit of the present season is very satisfactory.

## Export of essential oils

### a) from Messina:

	1900		1901	
	Quantity Kilos	Value Lire	Quantity Kilos	Value Lire
North German Ports . . . . .	22 014	286 182	13 676	205 140
Austria . . . . .	53 322	693 186	50 648	759 720
Belgium . . . . .	756	9 828	1 368	20 520
Denmark . . . . .	4 162	54 106	2 241	33 615
France . . . . .	37 310	485 030	36 312	546 195
United Kingdom . . . . .	214 721	2 791 373	211 342	3 170 130
Holland . . . . .	8 781	114 153	10 392	155 880
Russia . . . . .	7 845	101 985	9 331	139 965
Scandinavia . . . . .	4 445	57 785	6 216	93 240
Spain & Portugal . . . . .	1 257	16 341	1 064	15 960
Turkey . . . . .	1 250	16 250	1 560	23 400
United States . . . . .	291 227	3 785 951	266 614	3 999 210
South America . . . . .	985	12 805	3 510	52 650
Australia . . . . .	21 139	274 807	35 369	530 535
Egypt . . . . .	828	10 764	1 313	19 695
Greece . . . . .	319	4 147	360	5 400
India . . . . .	873	11 349	625	9 375
Malta . . . . .	80	1 040	60	900
Other countries . . . . .	2 290	29 770	500	7 500
Total:	673 604	8 756 852	652 602	9 789 030

### b) from Reggio:

Austria . . . . .	27 989	368 615	26 810	402 150
France . . . . .	24 558	323 429	24 315	364 725
North German Ports . . . . .	6 070	79 942	5 890	88 350
United Kingdom . . . . .	21 099	277 873	20 663	309 945
Malta . . . . .	40	527	200	3 000
United States . . . . .	28 297	372 671	27 440	410 100
Other countries . . . . .	290	3 819	415	6 225
Total:	108 343	1 426 876	105 633	1 584 495

### c) from Catania:

Austria . . . . .	1 499	19 487	1 650	24 750
United Kingdom . . . . .	460	5 980	350	5 250
North German Ports . . . . .	140	1 820	200	3 000
Other Countries . . . . .	—	—	210	3 150
Total:	2 099	27 287	2 410	36 150

### d) from Palermo:

Austria . . . . .	5 450	70 850	12 650	189 750
North German Ports . . . . .	3 290	42 770	13 15	19 725
France . . . . .	4 670	60 710	—	—
United Kingdom . . . . .	34 640	450 320	36 410	546 150
United States . . . . .	9 950	229 350	9 350	140 250
Other Countries . . . . .	560	7 280	612	9 180
Total:	58 560	761 280	60 337	905 055

### Total exports:

From Messina . . . . .	673 604	8 756 852	652 602	9 789 030
„ Reggio . . . . .	108 343	1 426 876	105 633	1 584 495
„ Catania . . . . .	2 099	27 287	2 410	36 150
„ Palermo . . . . .	58 560	761 280	60 337	902 055
Grand Total:	842 606	10 972 295	820 982	12 314 730

that is to say, in the year 1901, 21 624 kilos less, but an increase in value of 1 342 435 Lire.

The figures of the exports for the last ten years are as follows:

1892 359 378 kilos, value 5 543 358 Lire	1897 732 092 kilos, value 9 719 133 Lire
1893 588 334 „ „ 9 356 814 „	1898 667 293 „ „ 9 015 083 „
1894 666 740 „ „ 8 308 148 „	1899 797 145 „ „ 10 722 445 „
1895 554 191 „ „ 8 081 870 „	1900 842 246 „ „ 10 972 295 „
1896 514 067 „ „ 7 579 424 „	1901 820 982 „ „ 12 314 730 „

Referring to the individual essences, the results of the harvest of **Bergamot Oil** have fulfilled the expectations inspired by the good flowering period of the previous spring.

An abundant development of blossoms in the spring of 1901 had followed the low crop of the previous year, and the state of the weather during the summer was also very favourable for the growth of the bergamots. If the fruit had temporarily suffered through the heat-waves in July and August, the rainfall which occurred here and there allowed a more abundant irrigation of the gardens, so that the development of the fruit was not only not retarded, but a not inconsiderable quantity of new oil could already be shipped in the last months of 1901. Although it was due to the earlier commencement of the manufacturing season, that at first only oil with a low ester-content could be produced, the same cause prevented the price of the article from being driven up owing to scarcity of goods for prompt delivery. Oils with a higher ester-content did not appear on the market until towards the end of December, and only the essences produced in January and February of the present year reached an ester-content of 38—40 per cent.

The demand from abroad equalled the good results of the harvest, so that at the present moment the bulk of this year's oil has already been sold for consumption. The stocks still in the country are estimated at about 20—25 000 kilos, and as the new harvest can at the earliest only be expected in 7 or 8 months' time, it does not appear improbable that the quotations of this article will go higher in the course of the summer.

From the distillation-residues obtained in the rectification of bergamot oil, H. v. Soden and W. Rojahn<sup>1)</sup> have, in addition to bergaptene, isolated another crystalline compound in comparatively large quantity. This new body, melting at  $59.5^{\circ}$ , and, like bergaptene, odourless, has been named by the authors "bergaptin"; it belongs to all appearances to the aromatic compounds, and behaves like bergaptene, for example, it absorbs readily bromine, and is hydrolised by alcoholic potash solution into an acid which, when separated from the alkaline liquid by sulphuric acid, again passes over spontaneously into bergaptin. From this it may be concluded that in this body a ring-shaped closed atomic group is present, similar to that of coumarin. But the compound does not contain free hydroxyl groups or methoxyl groups.

G. H. Ogston and Moore<sup>2)</sup> have communicated the results of a series of observations, extending over a period of several years, on the physical properties of the oils of bergamot, lemon and sweet orange. It appears from the particulars, given largely in the form of tabulated statements, that there is in pure bergamot oils a constant relation between the specific gravity, the ester-content, and the optical rotatory power, so that any important deviation from this relation may always be taken as a sign that adulteration has taken place. The difference in the properties of oils pressed at various times of the year also appears clearly from these tables; they show how necessary it is to take this factor also always in consideration when judging a bergamot oil. The influence of unfavourable circumstances on the quality of the oil may also be gathered from the constants of some of the oils which had been pressed, at the commencement of the present manufacturing season, from unripe fruit blown from the trees by gales:

Specific gravity	Opt. rotation	Ester-content
0.8810	+ $16.3^{\circ}$	30.85 per cent
0.8789	+ $18.6^{\circ}$	26.70 " "
0.8819	+ $11.4^{\circ}$	32.25 " "
0.8808	+ $7^{\circ}$	30.95 " "
0.8816	+ $10.4^{\circ}$	32.9 " "
0.8812	+ $13.6^{\circ}$	28.65 " "
0.8833	+ $8^{\circ}$	33.5 " "

From the peel of a bastard fruit which does not attain ripeness, an oil is expressed, which is called "essence of black bergamot", and

<sup>1)</sup> Pharm. Zeitung **46** (1901), 778.

<sup>2)</sup> The Chemist & Druggist **60** (1902), 154.

which occasionally is used as an adulterant of bergamot oil. As it has a very dark colour, and, moreover, a fairly high specific gravity (up to 0.898) and low ester-content, detection should not be a difficult matter.

**Citron Oil.** Lemon oil and citron, cedro, or cedrate oil are still frequently mistaken one for the other, a fact which but a short time ago was proved in some reviews of a treatise dealing with citron oil, which appeared independent of each other in various journals. Although in most cases citron oil occurs in commerce mixed with oil of lemon, this does not justify the assumption that both oils are identical. To explain the matter once more briefly, lemon oil is obtained from *Citrus Limonum* Risso, and is called in Italy "essenza di limone", in France "essence de citron", and in Germany "Citronen- or Limonen-Oel". Citron, cedro, or cedrate oil, on the other hand, is obtained by expression from the fresh peel of *Citrus medica* Risso; in Italy it goes by the name of "essenza di cedro, or cedrino", in France by that of "essence de cédrat", whilst in Germany it is called "Cedro- or Cedrat-Oel".

H. E. Burgess has made the last-named oil the subject of an examination<sup>1)</sup>. In his opinion commercial citron oil is in most cases a mixture of the oils of lemon and verbena, with, it is said, occasionally small additions of rose oil. The oil examined by him, and designated by him as pure, had the following constants:

$$d_{15}^{\circ} = 0.8513; [\alpha]_D = + 80^{\circ} 13'; n_{D20}^{\circ} = 1.4750.$$

On fractionating at a pressure of 10 mm, 92 per cent of the oil passed over between 60 and 64°. On repeated distillation over sodium, a principal fraction was obtained, which boiled at atmospheric pressure at 173 to 174°, and consisted of limonene, which, on account of its low rotatory power (+ 89°) probably contained some dipentene. The portion passing over, at 10 mm pressure, between 64 and 85°, contained citral, and, accordingly, yielded, upon treatment with cyanacetic acid, citralidene-cyanacetic acid melting at 120 to 121°; the citral-content of the original oil was found, by the bisulphite method, at an average of 6 per cent, and by the hydroxylamine method at 5.7 per cent.

In the oil examined, a resinous crystalline mass had become deposited, from which, by dissolving it in chloroform, a crystalline compound  $C_{18}H_{18}O_6$ , melting point 145°, could be separated. This will probably be found identical with citraptene, examined by Crismer, and recently also by Theulier and Schmidt.

The same subject has been discussed by S. Gulli<sup>2)</sup> who recently made a communication on the adulteration of bergamot oil with oil

<sup>1)</sup> The Analyst **26** (1901), 260.

<sup>2)</sup> The Chemist & Druggist **60** (1902), 19.

of turpentine containing hydrochloric acid<sup>1)</sup>. According to the author, the following kinds of citrons are cultivated in the district of Reggio-Calabria and in Sicily:

1. *Citrus medica* var. *vulgaris* Risso, known in Calabria and in Sicily by the name of "cedro";
2. *Citrus medica* var. *gibocarpa* or *citrea* Risso, known as "cedrino", and
3. *Citrus medica* var. *rhegina* Pasquale, known by the name of "cedrone".

No distinction between these three kinds of citrons is usually made in commerce. The fruits, however, are not as a rule used for the production of the essential oil, but are exported in brine; the one most largely in demand is the "cedrone". Citron oil, therefore, is mostly only made specially to order in Sicily or in Reggio-Calabria at the time of the harvest; it is rarely found on the market in the pure state, as the manufacturers mix it with larger or smaller quantities of lemon or sweet orange oil.

An oil prepared last year by Gulli himself from "cedri" showed  $d = 0.8706$ , and  $\alpha_D = +67^\circ$ . These values agree fairly well with those obtained by us previously for citron oil<sup>2)</sup>, but they differ materially from those quoted by Burgess, so that the purity of the oil examined by the last-named does not appear to be quite above suspicion.

**Oil of Lemon.** In September last year the quotation of 1900 lemon oil, for prompt delivery, was about 6 Marks cif. Trieste, but large stocks were still held by speculators. The prices for oil from the new harvest, for forward delivery, were kept at about the same level; a rich crop was in view.

These low prices attracted general attention, especially from abroad, and a brisk business developed, both in spot and forward delivery. In spite of this the prices for prompt declined, as the speculators, on the approach of the new manufacturing season, endeavoured to dispose of their old stocks and replace them by new oil bought for forward delivery, so as not to have to realise their loss in old essence, but on the contrary carry the speculation on. Whilst the price of old oil thus fell, that of new oil was maintained at a high level. At the beginning of October a strong downward movement in the exchange with foreign countries set in in Italy, induced by the general favourable financial condition of the country. The price of lemon oil for

<sup>1)</sup> Report October 1901, p. 23.

<sup>2)</sup> Report October 1895, p. 13.

abroad comes higher when the exchange is low; but as the foreign countries, being already well supplied, were not inclined to pay higher prices, the owners of old essences, as well as the sellers of new oil for forward delivery, had no choice but to reduce the prices still further, in order to dispose of the old stocks and to secure a certain price for a portion of the new product. It thus happened, that the important gain of about 5 per cent in the rate of exchange, was lost by the fall in the prices of this article.

The manufacture commenced earlier than usual, as the blossoms had been abundant in April, and new ripe lemons were already to be had at the end of October. The fact, that foreign buyers had made large purchases of lemon oil only a short while before, led to an accumulation of stocks of new essence, and as, moreover, business in the fruit was very slack, an enormous quantity of lemons was available for manufacture, and more oil was placed on the market than is usual at that time of the year. The increase thus caused in the stocks, and the continued disinclination of foreign buyers towards a brisk demand for fruit in cases, have brought about a further decline in the prices. At the low rate of exchange a price of 5 Marks per kilo cif. Trieste represents a cost price of 1.35 to 1.40 Lire per Sicilian pound of 317 grammes, a price so low as has never been known before, however far one may look back through the price-lists of last century.

The opinions on the future movement of the article are divided; the Italian speculators have thrown themselves upon it with great energy, and have at the low prices taken a large quantity of the market, as they firmly believe that the prices in the course of the summer will go up by 20—30 per cent. People who look farther cannot help thinking that the immediate future of lemon oil, i. e. the course of the prices from next May onward, will be influenced exclusively by the more or less favourable prospects which the coming flowering period opens for next season's harvest.

If the blossoms are deficient, or only an average, in April and June, the speculators in Sicily will be able to obtain control of the article, and in that case excited moments may occur in the course of the second half-year of the present season. But if the prospects of the coming harvest should become favourable, large fluctuations would probably be out of the question, although in that case also a slow improvement in the prices is by no means improbable.

It is all the more difficult to give even only approximately correct figures of the stocks in hand, as the manufacture is still in full operation.

It is as yet equally impossible to say or even conjecture anything about the coming harvest. The trees are, however, in excellent condition; they have this year so far not suffered from heavy gales, and

show a good foliage. There have also been abundant falls of rain in the course of the winter, so that the agriculturist will have at his disposal a sufficient supply of water for the irrigation of the gardens, at the least throughout the summer months.

On the other hand, it cannot be denied that these preliminary conditions by themselves are not enough to guarantee a good harvest; the latter, on the contrary, depends principally upon the weather-conditions during the flowering season, i. e. from April till June. Strong and long-continued southerly winds, which often predominate in the spring and early summer, may have a very injurious effect on the germination of the blossoms, and injury of an equally serious character may be caused by rainy weather interrupted by hot summer days.

In conclusion the remark should be made, that, contrary to the experience of the last few years, when oils of bergamot and lemon on the average had a specific gravity below that which had formerly been considered a minimum, the normal figures of previous years again apply for the present season.

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In a detailed work on lemon oil, H. E. Burgess and J. F. Child,<sup>1)</sup> after mentioning some historical facts, discuss the cultivation of the lemon, and the manufacture, constituents, and examination of lemon oil. Up to the present, the following constituents have been detected: pinene, phellandrene, limonene, citral, octyl and nonyl aldehydes, geranyl acetate, geraniol, methyl ester of anthranilic acid, citronellal, citraptene, and a resin. The principal odoriferous agent of this oil is without doubt citral; but, according to Burgess and Child, a very important share in the production of the aroma belongs to the octyl and nonyl aldehydes, although these two compounds are only present in very small quantities.

Pinene, which has once before been proved (in our opinion wrongly) to be a normal constituent of lemon oil, has again been detected by Burgess and Child, and that in the form of the *lævogyre* modification. Although the physical constants of the fraction which contained this hydrocarbon did not completely agree with those of *l*-pinene, the authors consider the identity of their hydrocarbon with pinene as proved, as they succeeded in obtaining a hydrochloride melting at  $124^{\circ}$ . They attributed the isolating of pinene solely to the fact, that they were using a Young's twelve-beaded dephlegmator. Citronellal and phellandrene, however, were not detected by them in the material they examined.

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<sup>1)</sup> Journ. of the Soc. of chem. industry 20 (1901), 1176.

For the examination of lemon oil Burgess and Child consider it necessary to ascertain the following data: 1. the specific gravity at 15°; 2. the optical rotatory power in a 100 mm tube; 3. the index of refraction at 20° by means of Abbe's refractometer; 4. the citral-content, or the total content of aldehydes in 25 cc oil; and 5. they submit the oil to be judged to fractional distillation.

The average value for the specific gravity is given by the authors as 0,856—0,858; it is but rarely 0,860. The rotatory power of undoubtedly genuine oil fluctuates between +58° and +63°. The index of refraction is, in their opinion, a constant which may be found very useful in judging the oil; it fluctuates between 1,4733 and 1,4830. The most important part is the determination of the content of citral, or of total aldehydes; of the methods in use for this purpose, viz., the bisulphite, hydroxylamine, cyanacetic acid, and sodium sulphite processes, the first and last named are specially recommended, under certain definite precautions. According to the authors the citral-content amounts on the average to 4—7 per cent, and is only in very exceptional cases higher.

The principal adulterants of lemon oil may be considered to be lemon oil terpenes, turpentine and lemongrass oil citral, more rarely distilled lemon oil, cedarwood oil and stearin. The most difficult to detect are the lemon oil terpenes, as the natural oil contains already about 90 per cent of these. Less difficult is the detection of oil of turpentine. For the purpose of ascertaining foreign additions, Burgess and Child distil 100 cc oil at a pressure of at least 15 mm, and collect two fractions, one of 10 and the other of 80 cc, whilst a third fraction is obtained from the residue by steam distillation. The individual fractions are then examined for their rotatory and refractive powers (the latter in degrees of Zeiss' butterrefractometer). A typical distillation gives the following results:

Fraction	Passed over in min.	at mm pressure	Boiling point	$\alpha_D$	Refraction
1	7	14	64°	+55° 30'	72°
2	36	13	71°	+70° 40'	72.4°
3	—	—	—	+10° 56'	82.5°

In connection with this work Burgess and Child discuss the manufacture of a terpeneless lemon oil, for which they give the following average values: specific gravity at 15°, 0.895 to 0.899; rotatory power —5° to —8° 30'; index of refraction 1.4810 to 1.4822; total aldehyde-content not more than 50 nor less than 40 per cent.

What astonished us most in the foregoing was, that lemon oil is said to contain pinene, and this all the more, as we have repeatedly<sup>1)</sup>

<sup>1)</sup> Report April 1897, p. 20; October 1897, p. 26.

occupied ourselves with this matter, and always have been able to prove the absence of pinene. But on the strength of this communication we at once examined different samples from our stock, and we have as a matter of fact detected in the first runnings of each sample, (without requiring for that purpose a twelve-beaded Young's dephlegmator) a small quantity of a laevogyre hydrocarbon, which yielded a nitroso-chloride, and from that a nitrolbenzylamine which shows the same melting point as pinene nitrobenzylamine. This would no doubt point to pinene, and as the quantity of the nitrosochloride obtained is but very small, one could not even conclude that turpentine oil had been added purposely.

As this matter is of great importance for judging oil of lemon, — for it is a question whether under these circumstances the usual distillation test can be retained, — we will not, of course, remain satisfied with the tests already made, but, on the contrary, in the first instance examine a larger quantity of a product derived from an absolutely reliable source. We hope to communicate the result of that examination in our next Report.

In our Report of October last year we mentioned on page 25 a new aldehyde which H. E. Burgess had isolated from the terpene mixture obtained in fractionating lemon oil. As H. v. Soden and W. Rojahn stated shortly afterwards<sup>1)</sup>, it is not a question of only one, but of two aldehydes, and that probably nonyl and also octyl aldehyde. In spite of the small quantities of these bodies present in the oil — the authors only obtained a yield of 10 to 15 grammes from 10 kilos lemon oil, — v. Soden and Rojahn are also of opinion that these aldehydes are of a certain importance for the aroma of oil of lemon. They intend, however, to furnish conclusive proof that it is actually a question of nonyl and octyl aldehydes, and at the same time determine whether higher and lower homologous bodies are not also present in lemon oil.

We also notice the statement that, on shaking lemon oil with a solution of sodium bicarbonate, acidifying the solution with dilute sulphuric acid and extracting with ether, small quantities of acids can be isolated, which are partly volatile with water vapour, and partly not; the latter have a faint blue fluorescence, and are said to dissolve in alkali carbonates with a beautiful bright-blue colour.

at —————  
<sup>1)</sup> Berliner Berichte **34** (1901), 2809.

With oil of lemon (as Ogston and Moore discovered<sup>1)</sup>) a decided difference can also be detected between the oils pressed in different years, and what has been said under bergamot oil applies therefore equally in judging lemon oils. In most cases the specific gravity fluctuates between the limits 0.856 and 0.858, specially in the oils from the neighbourhood of Messina from Catania on the one side to Barcellona on the other. The oil exported from this district has a higher rotatory power than that obtained from the Palermo district, which differs from that from Messina in having a slightly higher specific gravity.

**Oil of Limes.** Jointly with H. Burrows, Tilden has again taken up<sup>2)</sup> his examination of the constitution of limettin which he commenced a long time ago. He had then obtained for this compound the formula  $C_{11}H_{10}O_4 = (OCH_3)_2C_6H_3 \cdot C_3HO_2$ , but now it was a question of clearing up the structure of the group  $C_3HO_2$ .

Dibromolimettin, which Tilden has described previously (but of which the melting point does not lie at  $257^\circ$ , as then mentioned, but at  $297^\circ$ ), yields on treatment with 10 per cent. potash solution, an acid  $C_{11}H_9O_5Br$ , which cannot be converted into a compound free from bromine, even when submitted to the further action of potash solution. As dibromocoumarin behaves in exactly the same manner, the supposition should not be rejected that the group  $C_3HO_2$  is constituted in the same manner as the lactone ring in coumarin. Dibromolimettin would then correspond to the formula:

$$(OCH_3)_2C_6HBr \begin{array}{l} \text{CH:CBr} \\ \text{O} \text{---} \text{CO} \end{array}$$
 and the acid  $C_{11}H_9O_5Br$  formed from it by the action of potash solution, would in such case be the corresponding coumarilic acid  $(OCH_3)_2C_6HBr \begin{array}{l} \text{CH=C} \\ \text{O} \end{array} \cdot CO_2H$ .

Similar to that of the dibromocompound is the behaviour of dichloro and trichlorolimettin; the latter yields a dichloro and the former a monochlorocoumarilic acid.

If limettin is heated in a water bath with a solution of sodium ethoxide, a sodium salt soon separates out; the silversalt formed from it, when heated with methyl iodide in a solution of methyl alcohol, is converted, under regeneration of a small quantity limettin, into a compound  $C_{12}H_{12}O_4$ , homologous to the latter, crystallising in needles of the melting point  $189^\circ$ , and which in its behaviour is very similar to limettin.

<sup>1)</sup> The Chemist and Druggist **60** (1902), 154.

<sup>2)</sup> Proc. chem. Soc. **17**, 216; after Pharm. Journal **67** (1901), 639.

**Oil of Orange, sweet.** In the autumn it was already pointed out that the anticipations of a very rich harvest had not been fulfilled, and that, on the contrary, a medium crop had to be recorded. If, in spite of this, the prices during September and October took a downward tendency, this must partly be attributed to the fact that at the beginning of the season the Italian fruit suffered an extremely severe competition from Spain (which had the advantage of the high premium on gold in that country), and that the export of oranges in cases looked far from promising. The growers were thereby induced to sell the fruit on the tree at low prices, and this was the cause that the manufacturers of essential oils had at first more material available than in previous years. As the fruit yields all the more oil, the less ripe it is when worked up, the manufacturing season commenced much earlier than before, and at a time when there was, as yet, no demand for the new article from abroad. For this reason the first oil met with a very cool reception on the market, and the manufacturers were forced to make concessions in the prices to the few purchasers. This led to an increase in the stocks, which depressed the price of the new oil more and more, until it reached such a low point that the manufacture became unremunerative. When about the middle of November the demand from abroad commenced, the prices improved gradually, which again enabled the makers to take up the manufacture. But as, at the same time, the opportunities for export of the fruit in cases became more favourable, it followed that only comparatively small quantities of fruit could be worked up, and the net result of the present season can only be called unfavourable. A tendency to higher prices seems therefore justified. The visible stocks are estimated at about 8 to 9000 kilos.

As communicated by Ogston and Moore<sup>1</sup>), sweet orange oil differs much less in its physical constants than the oils of bergamot and lemon. In most cases the specific gravity lies between 0.848 and 0.850, the optical rotation fluctuating from  $+ 96^{\circ}$  to  $+ 99^{\circ}$ . According to Ogston and Moore it is not true that the portion (10 per cent) first passing over in the distillation at ordinary pressure, has a lower rotatory power than the original oil. The authors observed always in the case of pure oil, that this fraction shows an average rise of at least one degree, and according to them, if the increase in rotatory power is less, there must be a strong suspicion that the oil has been adulterated either with oil of lemon or terpenes of lemon oil.

<sup>1</sup>) The Chemist and Druggist 60 (1902), 155.

**Estragon Oil.** The stocks of our own distillate, from plants grown by ourselves, will this year probably last until the new crop, even if there should be a demand for large quantities. Since we took up the distillation of this oil, the sale has increased five-fold. The principal consumption is for the manufacture of vinegar. One drachm of estragon oil is sufficient to impart a strong aroma to 20 gallons of vinegar.

It gives also excellent results in spice-mixtures for various dishes, soups, etc., used jointly with our distillates from the fresh leaves of parsley and celery.

**Eucalyptus Oil.** The trade in this product suffers from excessive overproduction, which, in spite of every warning, is carried on unflinchingly at the two principal sources of supply — Australia and Algiers — and which will lead to unpleasant consequences, if the production is not soon carried on in a more rational way.

The wonderful reports concerning the comprehensive therapeutic properties of this oil, which have been spread from Australia, have found little credence in Europe, but nevertheless the fact remains, that for example an epidemic outbreak of influenza causes an increased demand. In view of the important reduction in the price of eucalyptol, as the effect of the manufacture of this pure body on a large scale, the consumption may probably turn more and more towards the last-named article, as the common oil, owing to the content of various fatty aldehydes, causes disagreeable secondary actions on the respiratory organs, which render its use objectionable.

In our Report of October 1901, page 29, we mentioned the oil of *Eucalyptus Macarthuri*; of this oil we have since received a somewhat larger consignment. As the crude oil would probably find little use on account of its dark colour, we have submitted it to rectification in vacuo. In this process the bulk of the inodorous eudesmol which is contained in the oil, remains in the still, and only a small portion of this very readily sublimating body passes over into the distillate. The properties of the rectified oil differ very little from those of the crude oil, as will be seen by the following:

	Crude Oil	Rectified Oil
Specific gravity at 15°	0,9225	0,9175
Rotatory power	+ 1° 15'	+ 0° 21'
Saponification number	204,8 = 71,68% Acetate	211,3 = 73,95% Acetate
ditto after acetylation	240 = 80,5% C <sub>10</sub> H <sub>18</sub> O	244,2 = 82,2% C <sub>10</sub> H <sub>18</sub> O

It has a dark lemon colour, and forms a clear solution with 4 volumes 70 per cent alcohol, which also remains clear when more solvent is added.

We have included the rectified oil in our lists, and would recommend a trial, for example in compositions which contain geranyl acetate. The rectification improved the odour of the oil in a marked degree.

We have also received from Australia a small parcel of the oil of *Eucalyptus pulverulenta* Sims. This has a faint lemon colour, and a strong odour like cineol. Its specific gravity, at  $15^{\circ}$ , is 0.9217, the rotatory power  $\alpha_D = +1^{\circ}4'$ . The oil dissolves in two volumes 70 per cent alcohol, and gives only an extremely slight phellandrene reaction. It might therefore be taken into consideration as a substitute for Globulus oil.

R. T. Baker<sup>1)</sup> again makes us acquainted with a number of new species of eucalypts. For the botanical description we would refer to the original article; we only mention here those details which have reference to the essential oils obtained from the various species.

1. *Eucalyptus angophoroides*, sp. nov. (Apple Top Box). Yields 0.185 per cent essential oil, which in the crude state, at  $15^{\circ}$ , has the specific gravity 0.9049, and  $[\alpha]_D = -12.7^{\circ}$ . It contains much phellandrene, and also a small quantity of pinene. In the rectified oil, the eucalyptol fraction (= 70 per cent of the crude oil) contained only 26 per cent eucalyptol.

2. *Eucalyptus intermedia*, sp. nov. (Bloodwood or Bastard Bloodwood), yields only 0.125 per cent essential oil; this consists chiefly of pinene, and contains but little eucalyptol. Spec. gravity of the crude oil, at  $15^{\circ}$ , 0.8829;  $[\alpha]_D = +11.2^{\circ}$ . By its dextrogyration it differs from the oil distilled from the same material in the neighbourhood of Sydney, the latter being lævogyre to approximately the same extent.

3. *Eucalyptus lactea*, sp. nov. (Spotted Gum.). The essential oil obtained in a yield of 0.541 per cent contains no phellandrene, but at the same time such a small quantity of eucalyptol that it has no value as a commercial article. Specific gravity, at  $15^{\circ}$ , of the crude oil 0.8826, of the rectified oil 0.8788. The crude oil does not turn the plane of polarised light, but the rectified oil deflects it  $1^{\circ}$  in a 100 mm tube.

4. *Eucalyptus nigra*, sp. nov. (Black Stringybark). Like *Eucalyptus capitellata* it yields only an extremely small quantity of essential oil.

5. *Eucalyptus ovalifolia* (Red Box). Yield of oil 0.27 per cent. The oil contains much phellandrene, and only small quantities of

<sup>1)</sup> Proc of the Linnean Soc. of N. S. W. 1900, pt. 4.

eucalyptol; for this reason it is not suitable for commercial purposes. Specific gravity of the crude oil, at  $15^{\circ}$ , 0.9058;  $[\alpha]_D = -9.93^{\circ}$ . It differs in its composition but very little from the oil of

6. *Eucalyptus Fletcheri* Baker (Lignum vitæ, or Black Box) which is not suitable for commercial purposes on account of its large content of phellandrene and small eucalyptol-content. Yield 0.294 per cent specific gravity, at  $15^{\circ}$ , 0.8805;  $[\alpha]_D = -14.2^{\circ}$ .

7. *Eucalyptus polybractea*, sp. nov. (Blue Mallee). The oil obtained from this species belongs to the best oils distilled from eucalypts. The yield obtained in December amounted to 1.35 per cent. The crude oil has only a faint lemon colour; it has a strong odour of eucalyptol, and contains volatile aldehydes, as also free acids and esters only in small quantities. On fractional distillation 91 per cent of the crude oil passed over at below  $183^{\circ}$ , and this fraction contained 57 per cent eucalyptol; phellandrene could not be detected, but some pinene was present. The specific gravity of the crude oil, at  $15^{\circ}$ , amounts to 0.9143, that of the rectified oil 0.9109. In the non-rectified condition the oil is slightly lævogyre;  $[\alpha]_D = -2.13^{\circ}$ .

8. *Eucalyptus umbra*, sp. nov. (Stringybark, Bastard White Mahogany). Yield 0.155 to 0.169 per cent. Specific gravity at  $15^{\circ}$ , 0.8901—0.8963;  $[\alpha]_D +41.5^{\circ}$  to  $+43.8^{\circ}$ . Constituents of the oil are, much d-pinene, little eucalyptol, and also an acetic ester. Sapon. number 35.8.

9. *Eucalyptus Wilkinsonia* (Syn. *E. haemastoma* var. F. v. M.; *E. laevopinca* var. *minor* Baker). Yield of essential oil 0.9 per cent; specific gravity of the crude oil, at  $15^{\circ}$ , 0.894;  $[\alpha]_D = -23.9^{\circ}$ . No less than 86 per cent of the oil distil over at below  $170^{\circ}$ , and consist chiefly of l-pinene. At many different times of the year the oil contains small quantities of eucalyptol, at other times, however, some phellandrene; the oil contains moreover a small amount of ester.

10. *Eucalyptus Woollsiana* (Mallee Box). Yields on the average 0.495 per cent essential oil, which in the crude state, at  $15^{\circ}$ , has a specific gravity of 0.889, and  $[\alpha]_D = -13.7^{\circ}$ . This oil also contains but small quantities of eucalyptol, and has consequently no commercial value. The aromadendral, which was previously supposed to be cumic aldehyde, and which appears to be a characteristic constituent of the species of eucalypts designated as „Boxes”, is also present in this oil, but phellandrene could not be detected.

R. T. Baker and H. G. Smith<sup>1)</sup> have observed that the leaves of those species of eucalypts which yield oils with the same principal constituent, such as pinene, eucalyptol, or phellandrene, have corresponding venation. They even go so far as to accept that the principal constituent of a eucalyptus oil of which the composition is unknown, can be determined in advance by the venation of the leaves, provided that the type of the venation is already known from other species of eucalypts. Unfortunately we cannot reproduce in an abstract the details of this communication, equally interesting from a chemical as from a botanical point of view, and we must refer our readers for this purpose to the original article.

Several eucalyptus oils are distinguished by a pronounced peppermint odour; this is particularly the case with the oil of *Eucalyptus piperita*, which owes its name to this property of the distillate obtained from it. According to H. G. Smith<sup>2)</sup> the body which imparts the peppermint odour to these oils is present in the greatest abundance in the leaves of *Eucalyptus dives*, but also in those of other species, especially *Eucalyptus radiata*. The oils which contain this body are distinguished by the fact that they are at the same time rich in phellandrene. Smith prepared the compound in the pure state from the oil of *Eucalyptus dives*, and believes that it represents a ketone of the formula  $C_{10}H_{18}O$ . Further details on this subject will follow.

The same author has made a communication<sup>3)</sup> on a sesquiterpene, which is present in many eucalyptus oils in the portions boiling at more than  $255^{\circ}$ , and which, in the oil of *Eucalyptus haemastoma*, represents as much as 50 per cent of that fraction. It does not yield crystallised derivatives, but, on the other hand, when dissolved in glacial acetic acid, it gives characteristic colour-reactions with acids and also with bromine. When submitted to the action of bromine vapour the oil acquires first a carmoisin-red colour, then violet, and finally indigo-blue. The sesquiterpene prepared as pure as possible by fractional distillation, boils at atmospheric pressure at  $260-265^{\circ}$ , and has at  $19^{\circ}$  the specific gravity 0.9249. In support of the name *Aromadendrum* employed by Andrews for the genus *Eucalyptus*, Smith proposes for the sesquiterpene the name "aromadendrene".

<sup>1)</sup> Journ. and Proc. of the Royal Soc. of N. S. W. vol. **35** (1901).

<sup>2)</sup> Nature **65**, 192; according to Apotheker-Ztg. **17** (1902), 192.

<sup>3)</sup> Journ. and Proc. of the Royal Soc. of N. S. W. **35** (1901).

**Fennel Oil.** The prices of this article have hardened considerably during the last few months, as the stocks of Galician and Roumanian fennel seed are reported to be completely cleared. The price of the seed cultivated in the immediate vicinity of Miltitz is kept at such a high level, that, in spite of the high rate of carriage and import duty on the above mentioned foreign seed, the former does not enter into account for this season's distillation of fennel oil.

**Geranium Oils.** The distillers in Algiers now ride the high horse, and for prompt delivery demand prices which can only be obtained with difficulty, whilst at the same time large parcels for forward delivery are offered at lower rates. It is advisable at the present moment not to disturb the market by large purchases, but only to satisfy pressing requirements.

The direct export of geranium oil from Algiers to Germany amounted in 1900 to 1140 kilos. The total export of this article could unfortunately not be ascertained from the official statistical tables, but it may probably be calculated at not less than 10000 kilos.

The conditions in Réunion are still very difficult. Our agent writes under date 16<sup>th</sup> December 1901:

"On the 4<sup>th</sup> inst. the weather became stormy and a cyclone threatened, which, however, fortunately passed our island to the north without causing us great trouble. The only plant which has suffered from gales and rain is the geranium, of which the crop is completely destroyed. Serviceable new shoots cannot be expected for 2 or 3 months."

In order to satisfy our clients, we were compelled to have the oil purchased in small parcels. The quality of our imports was throughout faultless, a fact which cannot always be said of the parcels in the hands of foreign commission merchants. For the rest, there exists at St.-Denis, in Réunion, an official "*Laboratoire d'Analyses*" which issues certificates, but which confines itself prudently to the remark: "*D'après l'analyse chimique, l'échantillon examiné ne renferme pas de produits étrangers.*" (According to the chemical analysis the sample examined does not contain foreign products.) The total export of geranium oil from Réunion amounted in 1900 to 7137 kilos, value 302570 francs. In the year 1901, the export was in all probability distinctly smaller.

After passing through a most unpleasant period of scarcity, sufficient quantities of the so called East Indian geranium or palmarosa oil have, since the middle of December, at last again been imported. As far as our own imports are concerned, these parcels are throughout of exceptional quality. In fact, goods of equal value have not been on the market for a considerable time.

Almost worse still was the calamity in gingergrass oil, of which a passable grade was totally absent, and which could only be procured

in qualities of which the origin could hardly be detected. This extremely painful situation has been relieved since the middle of February. The quality of our present oil adds everywhere to our reputation.

**Guaiacum wood Oil.** As mentioned by us already some years ago,<sup>1)</sup> the parent plant of *Palo balsamo*, from which we distil our so called guaiacum wood oil, is, according to E. Paetzold, *Bulnesia Sarmienti* Lor. In his recently published thesis<sup>2)</sup> the author mentions *Palo balsamo* but briefly, and refers to a work which is to appear shortly in the "Archiv der Pharmacie". He deals more in detail with the resin and wood of *Guaiacum officinale* L. The matter which interests us is, that the bark of this tree yields about 1 per cent of an essential oil. From the resin a volatile oil could also be isolated, but this cannot be considered as an actual constituent of the resin, as its presence is explained by contamination of the resin with pieces of bark. Another fact worthy of note is, that a constituent which is present in genuine guaiacum wood in addition to the resin, i. e. the sticky guttin drawing out in long threads, yields dipentene when submitted to dry distillation. This terpene was identified in the product of distillation by the formation of its tetrabromide melting at 125°.

**Hop Oil.** We have transferred the distillation of this oil to our Bodenbach factory, which was in a position to acquire some small parcels of first-class Bohemian (Saaz) hops, very rich in oil. The South-German hops showed this year such a small oil-content as had never been observed before. If we had been dependent upon these, the price of the oil would be more than 400 Marks per kilo.

**Hyacinth "Schimmel & Co.".** The experience with this product continues favourable. It serves not only for the manufacture of hyacinth soaps and perfumes, but is also frequently used, jointly with rose and geranium oils, in the production of rose soaps. A point to be considered is the extreme richness of this preparation, as too large a dose might impair the effect.

**Jasmine "Schimmel & Co.".** The use of this perfume, which we were the first to introduce into commerce, has become more and more general. It may now already be counted among the most important auxiliaries of the perfumery trade, and it has recently also been improved to such an extent, that in quality it so nearly approaches the natural product, that, in dilution, the one can scarcely be distinguished from the other.

<sup>1)</sup> Report October 1898, 29.

<sup>2)</sup> Beiträge zur pharmacognostischen und chemischen Kenntniss des Harzes und Holzes von *Guaiacum officinale* L. sowie *Palo balsamo*, Strassburg 1901.

We would here mention specially, that our jasmine, even when kept for a long time, does not become dark, that is to say does not acquire that red colour which is sometimes so intense that it stains the manufactured products. We have seen samples of perfumes which had been mixed with another make, and which showed an intense purple-red colour.

A. Hesse continues his researches (adversely criticised by E. Erdmann<sup>1)</sup> on the development of the essential oil in the jasmine flower. In a new treatise Hesse<sup>2)</sup> answers first of all Erdmann's criticism, and explains once more that, contrary to the latter's statement, the oil obtained by extraction from fresh jasmine flowers does not contain methyl ester of anthranilic acid. He shows again, with a "jasmin pur" supplied by Pillet under guarantee of purity, that methyl anthranilate is not present in demonstrable quantity in the extract of jasmine flowers. For this reason Hesse believes that he must maintain his opinion that this ester is formed during the enfleurage process. Possibly it may be explained by the decomposition of a complex nitrogenous compound. A number of long-known observations are in favour of such a possibility, — observations, which have proved experimentally the formation of odoriferous matter by decomposition of an inodorous compound.

E. Erdmann's objections to the experiments made by A. Hesse with the view of determining the various yields of oil by enfleurage and by extraction of jasmine flowers, point to the fact that Erdmann has not recognised the essential difference between these two processes.

The advantage of the enfleurage method over the other processes which may be employed for obtaining jasmine oil from the flowers, are shown in a tabulated statement. From this it appears that 1000 kilos fresh jasmine flowers do not yield a larger quantity of oil when submitted to the processes of extraction and distillation, than the quantity still present in the waste flowers which remain after treatment of the same quantity of flowers by enfleurage. If these results clearly show that during the enfleurage process essential oil is formed in the picked flowers, the question yet remains to be answered, wherefrom do indol and methyl anthranilate subsequently originate, bodies which at first are evidently not present in the free state in the fresh flowers?

When the fresh jasmine flowers were stored in an open room, no increase in the content of essential oil could be detected.

The oil obtained from these flowers by distillation contained anthranilic acid ester, but no indol.

<sup>1)</sup> Berl. Berichte **34** (1901), 2281. See also our Report of October 1901, 33.

<sup>2)</sup> Berl. Berichte **34** (1901), 2916.

To these experiments by Hesse, Erdmann<sup>1)</sup> replies, in a note on oil of jasmine flowers, that the informations which A. Hesse has thought fit to address to him on the subject of the enfleurage method, are superfluous. The fact that Hesse has misunderstood him must be attributed to the somewhat obscure ideas which Hesse has formed about a difference in the capability of the fat to dissolve odoriferous matter, or to absorb it and condense it upon itself.

According to Erdmann's interpretation, the products obtained by the two methods must be considered as two different fractions of one and the same oil. He has nothing to say against the supposition that the odoriferous substances represent occasionally the product of decomposition of complex bodies, but what only appears to him incredible is Hesse's first opinion, that the increase in the odoriferous substances of the jasmine flower is due to a process of vegetation which still continues after the flowers are picked. Erdmann maintains now as before that the experiments made by Hesse are not suitable for proving the new formation of jasmine oil during the enfleurage.

Contrary to Hesse, Erdmann has succeeded in isolating and crystallising blue fluorescent methyl ester of anthranilic acid from an oil obtained in 1898 from jasmine flowers by the extraction process. It was identified a little further by conversion into an azo-colour and the platinum double salt. The jasmine extract examined was obtained from the firm Roure-Bertrand fils, who declared that the extract had been produced without the addition of orange flowers. The author has no reason to doubt this statement.

**Lavender Oil.** There has lately been no change in the value of this product, which belongs to the most important articles of the perfumery industry. A splendid selection of qualities can now be had at very low prices.

Since many years we have already been buying the lavender oils direct from the producers, through a commission agent specially appointed for the purpose, who has the advantage over the ordinary brokers of the South of France of being a chemist and capable of conducting the examination of the parcels offered to him according to our own system. This gentleman is personally acquainted with the producers of the different departments, and consequently buys at first hand. According to agreement he charges us cost price, and is only allowed the usual commission and the cost of repacking. A similar arrangement has also been made for other products from the South of France.

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<sup>1)</sup> Berl. Berichte **35** (1902), 27.

Our position is consequently as favourable as it is possible to be, having no expenses of own management, and not being bound to disregard opportunities which may possibly offer themselves in other departments of Provence. The general search for direct sources of demand has also taken hold of the small distillers of essential oils, who formerly sold their products to Nîmes, Grasse, Cannes and Nice and whose localities have in recent years been linked by railways to the main traffic of the world. This has led to a complete re-arrangement of the supply, and the assertion that from here we buy the oils of Southern France as cheaply as the firms in the towns mentioned above, is a fact which is proved by our quotations.

The map of the lavender and spike districts of the South of France, which accompanies the present Report, should prove that we have a sufficient knowledge of this territory to cope with any competition. By means of exact statistics we keep a constant check where the finest oils, richest in ester, are distilled.

A high scientific authority in Montpellier mentions, with regard to this map, that in the departments Gard and Hérault, on the right bank of the Rhône, very little lavender oil is distilled, but that, on the other hand, these departments are the principal sources of production of spike oil.

In the mountainous district from Le Vigan to Bleymard (Lozère), and also on the mountains east of Viviers, a little lavender oil is distilled. These quantities are, however, of quite secondary importance, as compared with those which are distilled on the left bank of the Rhône.

We have repeatedly<sup>1)</sup> been compelled to refer in our Reports to attempts made with the view of artificially raising the ester-content of lavender oils. This time we are again in a position to mention such an attempt; in this case it is a question of a lavender oil which had been mixed with benzoic acid in order to raise the saponification number.

This new adulterant has not been selected badly as such, because it does not affect the physical constants of the oil, as is shown by the following figures, and the oil in question is only suspected on account of a low acid number.

Two samples of lavender oil behaved as follows:

$$\begin{aligned} \text{I.} \quad d_{15^{\circ}} &= 8886 \\ a_D &= -6^{\circ}. \end{aligned}$$

<sup>1)</sup> Comp. our Reports of April 1897, 24, and October 1900, 41.

Soluble in 2 to 2.5 volumes and more 70 per cent alcohol.

Acid number = 6.6,

Sapon. number = 82 = 28.7 per cent ester.

II.  $d_{150} = 0.8884$ ,

$\alpha_D = -6^\circ$ .

Soluble in 2 to 2.5 volumes and more 70 per cent alcohol.

Acid. number = 6.8,

Sapon. number = 79.74 = 28 per cent ester.

Whilst otherwise lavender oils are almost neutral, the acid number shown rendered the quality of this oil doubtful, and induced us to isolate the free acid. For this purpose the oil was shaken in a separating funnel with a dilute solution of soda, the latter then separated from the oil, acidified with dilute sulphuric acid, repeatedly shaken with ether, and the ethereal solution evaporated. The residue consisted of a yellowish-brown mass, which could be recrystallised from water, and yielded white crystals. As the latter sublimed on being heated, the whole mass was purified by sublimation, which resulted in fine crystalline needles of the melting point  $120^\circ$ .

On account of these properties, as also by the reaction with ferric chloride, the acid had already been recognised as benzoic acid; but for more exact identification the silver salt was also prepared and analysed:

0.667 g silver salt yielded 0.3144 g Ag.

Calculated for  $C_6H_5COO Ag$ :

Found:

47.16 per cent Ag.

47.14 per cent Ag.

We may add that the benzoic acid detected in the lavender oil contained chlorine, and was therefore an artificial product. This proves that in the present case it was a question of adulteration, and not of a natural constituent of the oil.

The acid number obtained indicates an addition of benzoic acid of about 1.5 per cent. This proportion as such is small, and it would appear that the process of adulteration is to some extent only in its infancy. The intention has probably been to try whether it would be detected or not, and in the latter case gradually to become bolder.

The occurrence, however, again proves how necessary it is to be constantly on the alert. It also helps to realise in what condition the trade in essential oils would now be, if science did not provide such a firm support.

**Lemongrass Oil.** The state of the market of this article during the last half-year was again very animated. Whilst in August the price was about 12 Marks, it rose at the beginning of October to about 15 Marks; in the middle of that month it stood already at 18 Marks, in December at 20, and in January of this year it reached

the highest level at 21 Marks. From that time an unimportant backward tendency set in, but only for spring shipment, whilst spot cannot yet be bought cheaper, but, on the contrary, is in demand at the present quotations.

When judging the value of this oil, it should be taken into consideration that now for some years very considerable quantities of lemongrass oil have been used in the manufacture of citral. It would therefore appear out of the question that it will ever go back to the former price of 6 Marks per kilo, as an increase in the production corresponding to the greater consumption is not apparent, in fact, the following table shows that the exports have decreased considerably:

Export of lemongrass oil from Cochin, Malabar Coast.

	From	1 <sup>st</sup>	July	1900	to	30 <sup>th</sup>	June	1901:	23 196	bottles <sup>1)</sup>
against,	"	1 <sup>st</sup>	"	1899	"	30 <sup>th</sup>	"	1900:	33 504	"
	"	1 <sup>st</sup>	"	1898	"	30 <sup>th</sup>	"	1899:	39 458	"
	"	1 <sup>st</sup>	"	1897	"	30 <sup>th</sup>	"	1898:	37 788	"

Through the courtesy of the Government Laboratory of Antigua, W. I., we recently obtained a sample of lemongrass oil which had been distilled in that island; it had the following constants:

$$d_{15}^{\circ} = 0,8956; \quad a_D = - 0^{\circ} 11'.$$

Aldehyde-content: 76,5 per cent (bisulphite process).

Insoluble even in absolute alcohol.

In its properties the oil agrees in a remarkable manner with a Brazilian oil which was sent to us years ago;<sup>2)</sup> both oils are unable to compete with the East-Indian oil, above all on account of their insolubility in alcohol. The question arises, whether the difference is due to climatic conditions, or to the manner of distillation?

**Neroli "Schimmel & Co."** The results constantly to be placed to the credit of artificial neroli oil (invented by us) in its struggle with the natural product, have recently become specially pronounced. It is quite clear that the prejudices which have existed in this case, like in those of all other novelties, are disappearing before the knowledge that it is here a question of a first-class product, on the eminent qualities of which all criticism must come to grief.

It is now accepted as an established fact, that the perfumery trade possesses in the artificial neroli oil a help of remarkable value, the liberal use of which is a matter of great advantage. Whether the distillers in Southern France are right or not in maintaining that after

<sup>1)</sup> Wine bottles of 620 grammes capacity.  
<sup>2)</sup> Report April 1896, 63.

all there does exist a difference between the two products, this much is a certainty, that such a difference would rather be in favour of the artificial neroli, than against it. It is well known that the quality of natural essential oils is frequently improved and rendered finer by the abstraction of certain bodies. We would only refer to the removal of terpenes, sesquiterpenes, fatty aldehydes, etc., to show that natural products *per se* are not always perfect, on the contrary, frequently want improving in order to meet the requirements of the perfumery trade. The conspicuous performances of perfumery, as we now see them in the products daily before our eyes, are without doubt in no small degree due to the use of improved materials and ingredients, in harmonious co-operation with a refinement of the taste. It is evident that our artificial neroli oil is a product which offers great advantages to the perfumery trade, for it enables the perfumer to employ on a liberal scale the fragrance of orange blossoms which was formerly considered one of the perfumes of luxury. To those who have not yet bestowed their sympathies upon the artificial oil, we would appeal for a trial, for which we shall be glad to supply samples.

Like every one of the new products which we have during the last few years introduced into commerce, this one is also frequently imitated and offered at very low prices. Such spurious goods have nothing in common with our original product, as the composition of the latter is our secret.

**Orange Flower Oil.** P. Jeancard and C. Satie<sup>1)</sup> report on the properties of the oils of orange flowers and petitgrain of the last harvest. The specific gravity of the neroli oils examined was between 0,8660 and 0,8684 (27°), the optical rotation between  $+5^\circ$  and  $+1^\circ 50'$ . The saponification numbers fluctuate between 30,1 and 53,2. The solubility in 80 per cent alcohol was 1 in 1,5 to 1,8, at 25°. The authors further determined the saponification number by cold process, specific viscosity, and surface tension. For petitgrain oils the following constants were obtained: specific gravity at 26° = 0,8820 to 0,8830; rotation  $-4^\circ 50'$  to  $-5^\circ$ ; solubility in 70 per cent alcohol 1 in 3,0. The saponification numbers were between 150,5 and 158,9.

In comparison with the previous year's oils, the neroli oils of the last harvest show therefore only a small increase in specific gravity. Rotatory power and saponification number, however, agree fairly well with those of the previous year's oils. The petitgrain oils have a somewhat lower specific gravity than in the previous year. The optical rotation shows less important deviations; the saponification numbers are approximately the same.

<sup>1)</sup> Bull. soc. chim. III, 25 (1901), 934.

In the "Journal für praktische Chemie" vol. 64 (1901), 245, A. Hesse and O. Zeitschel communicate some observations made during a comparative examination of the processes for obtaining the aroma of orange blossoms, which are in use in the South of France. In the distillation of the blossoms a portion of the oil, as is well-known, passes over into the water, which under the name of orange flower water is used on a large scale. The authors, by exhausting the distillation water with ether, have determined the quantity of the oil passing over into the water, and have found that it represents about one third of the total amount of oil from the orange blossom.

The specific gravity of the water-oil is 0.950, at  $15^{\circ}$ ;  $\alpha_D = +2^{\circ}0'$ ; sapon. number 72. The content of methyl ester of anthranilic acid is remarkably large, i. e., 16 per cent, from which it may be concluded that the content of anthranilic acid ester in the total quantity of the oil from orange blossoms is about 5 per cent, whilst in ordinary neroli oil rarely more than one per cent of this ester has been found. The total quantity of oil obtained from orange-flower pomade, by a process which we have already mentioned on a previous occasion, had the specific gravity of 0.913 at  $15^{\circ}$ ;  $\alpha_D = -5^{\circ}$ ; saponification number 78; content of methyl ester of anthranilic acid = 9.2 per cent. It was here found, that the blossoms macerated with fat, still contained some oil, which, upon distillation of these waste blossoms, partly separates out as oil on the distillation water, and partly remains in solution in the latter. The former contains only 0.35 per cent, but the latter, obtained by repeated shaking with ether, 8.85 per cent methyl ester of anthranilic acid.

The total oil obtained by extraction of orange blossoms with volatile solvents had the specific gravity of 0.907 at  $15^{\circ}$ ; sapon. number 55.2; content of anthranilic acid ester 7.6 per cent. Enfleurage of orange flowers (a process little used in practice) yielded but a small quantity of oil, whose constants were: specific gravity 0.909 at  $15^{\circ}$ ;  $\alpha_D = -8^{\circ}34'$ ; sapon. number 58.2; content of anthranilic acid ester, 5.2 per cent. With orange blossoms the enfleurage method gives the smallest yield, as compared with the other three methods; with jasmine blossoms, however, the reverse takes place. In the saponified oil of orange blossom water, phenyl ethyl alcohol, phenylacetic acid, and geraniol were detected.

The authors also made experiments to test the stability in boiling water of the esters which come chiefly under consideration for oil of orange blossoms, viz., linalyl acetate and methyl ester of anthranilic acid.

It was then found that methyl ester of anthranilic acid does not become decomposed at all, whilst of linalyl acetate, after three hours boiling with water, about 20 per cent had decomposed into linalol and acetic acid.

The physical constants of the pure linalyl acetate used for these tests and produced by Tiemann's process, were: boiling point 115 to 116°, at 25 mm; specific gravity 0.913 at 15°;  $[\alpha]_D = -6^\circ 35'$ ; ester-content 97.6 per cent.

In our Report of April 1893 we referred already, on page 30, to the facility with which linalyl acetate is decomposed when boiled with water; we then mentioned that bergamot oil containing 40 per cent linalyl acetate, after steam distillation only contains 22 per cent ester.

The property of methyl ester of anthranilic acid, as a primary aromatic base, of forming azo-dyestuffs may be utilised according to E. Erdmann<sup>1)</sup> for the detection and quantitative estimation of this body in essential oils. For this purpose, the diazotised solution of methyl ester of anthranilic acid, made up to a definite volume, is titrated with an alkaline solution of  $\beta$ -naphthol, when the dyestuff formed is precipitated. The presence of methyl ester of methylantranilic acid, which during the reaction passes over into the nitroso compound, does not affect the estimation. The process, illustrated by several examples, gives satisfactory results.

In a jasmine extract obtained in the year 1898 from Roure-Bertrand Fils of Grasse, the presence of methyl ester of anthranilic acid could by this method be demonstrated; 100 grammes of the extract contained only 0.00741 gramme of this ester.

**Orris Oil.** The situation of the Florentine orris-root market is described in the following special report which we received from one of the principal interested parties.

"Since our previous reports, our views on Florentine orris-roots have practically remained the same. At the same time it is surprising that, in spite of the low prices, the purchases from abroad have not increased to such an extent as might have been expected, in consequence of which very important quantities have remained unsold and in the hands of merchants. The present prices asked for first quality Florentine orris-roots assorted, fluctuate between 45 and 50 Marks cif. Hamburg; at the former figure small parcels might be purchased, whilst large quantities are dearer. With regard to pickings, most of the owners have sold these separately, as this quality has always been most in demand, and it would therefore be a difficult matter to obtain a large quantity without forcing up the price. The question might otherwise shape itself thus: for example, if a large harvest could be relied upon, in view of the state of the next flowering season, the owners, who at this moment are in no hurry to sell, might then presumably be prepared to make fresh concessions, which would force the price of the assorted regular quality further back, and bring it nearer to the price paid for the pickings. Naturally, the further attitude of the foreign buyers will be an important factor in the situation. With regard

<sup>2)</sup> Berliner Berichte 35 (1902), 27.

to the result of the prospective harvest, judged from the present situation, it has to be borne in mind that the rhizomes then maturing represent the product of the cultivation of the autumns of 1899 and 1900, which was everywhere conducted on a large scale, owing to the remunerative prices then ruling. As is well known, the roots can already be gathered after two years, but after three years they are more fully developed, and the yield in weight is consequently more advantageous. On the other hand, the roots must not be left in the ground after the end of the third year, as they would otherwise deteriorate or decay. During the last autumn (1901) the roots gathered were very largely only those planted in 1898, whilst the 1899 cultivation, on account of the low selling prices, was mostly left undisturbed. For this reason the last harvest only amounted to about 700000 kilos instead of 1000000 kilos or even more, as the previous estimate was. Next autumn the three-year roots will probably again be gathered by preference, and the two year old roots left undisturbed, as a real improvement in the prices can hardly be expected in face of the large stocks of previous harvests, and no remunerative business for the producers can be anticipated. The cultivation of last autumn points to a decline, as compared with the two previous years, and next autumn it will no doubt be still further restricted on account of the bad experience of the producers. It is therefore possible that in the course of time the natural consequence of the present decline in the values of this product will follow, that is to say, smaller harvests, and as a logical sequence, better prices."

The foregoing no doubt makes it clear that in the near future no higher prices of orris-roots and the products thereof need be feared, and that the perfumery trade will in all probability for some time to come be able to derive a considerable advantage from the present low values.

In our new Works the manufacture of orris oil on the largest scale has been specially provided for. It takes place in rooms where besides this only roses and sandalwood are distilled, and where in every respect the delicate character of the violet aroma has been fully taken into consideration.

The liquid concentrated orris oil "Schimmel & Co.," first introduced into commerce in April last year, has meanwhile, by further perfecting the quality, been brought by us to the ten-fold concentration of ordinary solid orris oil. It has already led to numerous imitations.

This oil is a violet perfume *par excellence* and a dangerous rival of ionone, over which it has the advantage of greater persistency and uniformity of aroma. When comparing the richness, the considerable difference in the prices should be taken into account.

**Patchouli Oil.** This article had for a long time been offered at ridiculous prices, when suddenly a general reduction of stocks became apparent, which led to frequent speculative purchases and caused a certain amount of excitement on the market. In the meantime the disposition has become more quiet, and if the large consignment of patchouli leaves, which is now on the way for us from Penang, should have the usual normal content, we shall shortly be able to supply

our own distillate again at essentially lower prices. We would therefore recommend our customers not to conclude at this moment large purchases of this article; at the same time we are in a position to supply promptly all current requirements.

**Peppermint Oil (American).** The doubts we expressed whether the rise in prices would attain the dimensions hoped for by the speculators, appear, unfortunately, to have been without justification. The speculators were correct, and as early as November last year no good quality crude oil could be bought below \$ 1.80 to about \$ 2.— per lb. taken at New York. Since that time the prices have been kept at the same level, and the market is just in that condition, that an increase in the demand will cause a further rise in the quotations.

On the whole the farmers and producers are entitled to the improvement in the value, for they have been working at a loss for years. It is no less in the interest of the consumers of peppermint oil, for this reason, that when the producers ceased to take an interest in the industry, the cultivation was no longer conducted with the care of former years, a fact which, naturally, had an unfavourable effect on the general quality of the oil. This was the cause that in 1899 and 1900 much inferior oil was produced, for at prices of 75 to 80 cents per lb. oil, all expenditure for clearing away the weeds, and manuring the fields, had to be avoided, or at least cut down to the lowest possible limits. This would also explain the complaints about the quality of the American oil, made during that period in Europe.

But another important factor in favour of a continuation of the present prices is this, that several of the large producers, encouraged by the rising market, combined in the course of last autumn, purchased nearly all the oil held by the smaller distillers, and in a short time were able to control the market completely. This combination is considered strong enough to maintain the present situation in case the demand should fall off, and that all the more readily, as the expectations of the new harvest, although this is still very far removed, are not favourable.

According to the latest reports from our New York branch, which has now for 32 years carried on the trade in peppermint oil as a speciality, the above represents the opinion prevailing in America. The rest must, naturally, be left to the future.

**Peppermint Oil, Japanese.** With regard to the value of this product, the same applies, in a general way, as what we have said about menthol on page 97 of this Report. As a rule the prices of the natural oil do not correctly correspond to those of menthol crystals, whereas the dementholised oil is always, comparatively speaking, very inexpensive. The latter is used chiefly for cheapening the inferior

kinds of oil. But on account of its bitter, oily taste, it can only be used for the cheaper kinds of confectionery.

Export of peppermint oil from Yokohama and Kobe,  
from 1<sup>st</sup> August to 31<sup>st</sup> December 1901.

to Hong Kong . . . . .	23 715	catties
„ Hamburg . . . . .	5 355	„
„ London . . . . .	2 925	„
„ Havre . . . . .	1 800	„
„ Bombay . . . . .	152	„
„ Madras . . . . .	60	„

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Total 34 007 catties,  
or about 20 400 kilos.

Total export of peppermint oil from Japan,  
in the year 1901.

From 1 <sup>st</sup> January — 31 <sup>st</sup> July . .	18 606	catties
1 <sup>st</sup> August — 31 <sup>st</sup> December	34 007	„

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Total 52 613 catties  
or about 31 550 kilos.

According to recent reports from Japan, a fall in the prices is not considered probable.

**Peppermint Oil, Mitcham.** We hear from our London Branch, which negotiates our purchases of crude oil, that the stocks of pure original distillates held at first hand have dwindled considerably, and that it would at this moment be difficult to hunt up some few thousand pounds of these qualities. The best parcels usually pass into firm hands soon after the harvest. The prices of those goods cannot be touched, but inferior commercial qualities can be had in any quantity, and nobody knowing the state of affairs will be surprised at the enormous differences in the selling prices charged by middlemen. We supply only the best quality in existence; for the consumer, nothing is easier than to cheapen the article himself, by mixing it with American oil.

E. Charabot and A. Hébert<sup>1)</sup>, in continuation of their previous examinations<sup>2)</sup>, have studied the influence of fertilisation with common salt on the development of the plant. They found that from a certain stage in the development, the water-content of the plant diminishes and the content of organic substances is thereby increased, no matter whether the plant developed normally, or under the influence of the

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<sup>1)</sup> Compt. rend. 134 (1902), 181.

<sup>2)</sup> Compt. rend. 132 (1901), 159.

salt. In the latter case the changes are much greater. With regard to the oil produced by the plant, it was found that when the development of the plant progressed normally, the content of menthol esters increased, but that of menthone diminished. Chloride of sodium promotes the process considerably, but in spite of this it retards the development to such an extent, that the yield of ester per acre is less than in the case where the plant has developed in a normal manner. The two investigators, however, quote only the result of one experiment as a proof of their observations.

**Petitgrain Oil (Paraguay).** We have received the following original report on this article and on the causes of the serious depreciation during the last six months:

The manufacture is carried on in small factories in the immediate vicinity of orange forests, as the total absence of all means of communication renders it impossible to centralise the production. Every group of factories is managed and superintended by one employee. The woods have always the character of timber forests of the most diverse varieties, among which is found a sort of undergrowth of smaller dimensions, with patches almost completely covered with orange trees, which the inhabitants call *manchones*. Such *manchones* are scattered about the forests at certain distances.

In specially favourable situations the *bigaradier* predominates, in others the latter is found mixed with the sweet orange and with another species called *assessii*, which is a variety of the two first-named. This species is used preferably for the manufacture of petitgrain oil.

Although the orange forests are very numerous in Paraguay, they afford but rarely the preliminary conditions necessary for normal working, as they are mostly far removed from inhabited centres. The leaves are gathered all the year round, but chiefly between October and April, during which period the bulk of the oil is produced. For this purpose the trees are cut down at a height of about 2 inches from the ground; the leaves and young fruit are distilled together, and the wood of the trees is used as fuel for the boiler. This indiscriminate clearing, which must be attributed to the indolence of the inhabitants, has led to the complete destruction or exhaustion of large tracts, which produce so little that the manufacture there only pays when the prices of essences are exceptionally high.

The present situation is as follows: When, owing to exceptional circumstances, such as the outbreak of bubonic plague, the closing of the ports, and insufficient production, the prices of essences had reached an abnormal height, many persons, who 7 or 8 years ago exported the essence, again took the article in hand. The high prices paid by them led to a greatly increased production, which reached the culminating point in April 1901; in July, however, it had already gone down again considerably. Meanwhile the production has much exceeded the normal requirements. The slump has been caused by circumstances which have absolutely no connection with the production. Its causes must rather be attributed to the fact, that most of the exporters are compelled to draw bills for the greater portion of the value of their shipments, and the proprietors in Europe are now anxious to realise the goods and thus recover the money advanced. Moreover, some independent producers in Asuncion have made the situation worse by shipping the essence under different brands, and appointing agents in a great number of European towns to hawk the goods about.

The enormous depreciation which has thereby been brought about, has, naturally, led again to restriction in the production. For the rest, the prodigious quantities offered from some quarters in Europe exist only in the imagination of the parties concerned, and prove that the latter have not the faintest idea of the real volume of the production.

Under these circumstances the advice to consumers can only be, to take advantage of the present low quotations by laying in stocks sufficient for many a day. But it cannot be recommended to buy ahead for still longer periods, as the quality of the essence deteriorates when it has reached a certain age.

The total production of Paraguayan petitgrain oil in normal years is estimated at about 12 000 kilos. In the year 1901 the total exports from Paraguay, according to official figures, amounted to 9 545 kilos, value 14318 gold pesos.

**Pine Needle Oils** are, on the whole, unchanged, but a distinct increase in the consumption can be recorded, which the production during the winter may possibly not completely meet. The extra-fine grade distilled from cones is fairly scarce, and we have only succeeded with difficulty in obtaining the quantity required for the current demand.

The Siberian oil is constantly growing in favour, and can be supplied in any quantity. The genuine oil from *Pinus pumilio* is comparatively cheap, and is in stock in the well-known excellent quality. The same applies to the fragrant oil distilled from the young needles of *Abies pectinata*, which is preferred for the finer perfumes of the forest odours.

**Rose Oil (artificial) "Schimmel & Co."** This product, which, thanks to the results of our most recent investigations, has now reached the highest degree of perfection, has a constantly increasing consumption. By its help new possibilities have been opened for the practical application of the rose odour on a large scale, and also for less valuable products, possibilities of which the manufacturers of perfumes and soaps are now becoming fully aware. After the improvements made in our artificial rose oil by the addition of various hitherto unknown constituents of the natural oil of rose, and in view of the probability that at the present time all the more important bodies which jointly produce the rose odour have been discovered, our rose oil should no longer be considered as a make-shift, but may now with full right be called a perfect substitute for the natural product. No one, who has seriously compared it with Turkish rose oil, disputes this claim.

A special favourite of perfumers, tobacco manufacturers and others is the liquid oil, free from stearoptene, which is about 10 or 12 per cent richer than the product containing stearoptene, and which moreover has the great advantage of forming solutions which remain clear under all conditions of temperature. For these reasons the perfumer should use the oil free from stearoptene.

In cases where the oil as an article of commerce is competing with the commercial Turkish qualities, it is, naturally, only the oil containing stearoptene, whose congealing point is approximately equal to that of the Turkish oil, which comes under consideration.

Since the publication of our last Report, a German Patent (No. 126736) for artificial rose oil has been granted to us. An artificial oil of rose containing the bodies discovered by us, may therefore neither be offered by other firms, nor be purchased, — a fact to which we would hereby draw attention.

During the rose harvest of the summer of 1901, H. v. Soden and W. Rojahn<sup>1)</sup> have made experiments to ascertain the content of phenyl ethyl alcohol in rose blossoms.

In order to obtain the whole of the oil, they extracted with ether the water passing over with direct steam in the distillation of 50 kilos rose blossoms, and obtained in this manner 37.5 grammes oil of the specific gravity 0.944, at 30°. In the distillation of this crude oil with water vapour, it yielded about 10 per cent rose oil of the specific gravity 0.845, at 30°, of which the properties corresponded generally with ordinary rose oil containing only a small quantity of phenyl ethyl alcohol. The bulk, i. e. 67.5 per cent of the crude oil, passed over in the water during the distillation, whilst 13.5 per cent were represented by residue and loss. The oil which had passed over in the distillation water consisted chiefly of phenyl ethyl alcohol. Similar results were obtained with rose blossoms from which the calyces had previously been removed, when it was found that the calyces distilled separately also yielded a small quantity of oil.

The result of these experiments is that the total crude oil of the rose blossom, obtained by distillation with direct steam and extraction of the distillation water with ether, consists for 50 to 60 per cent of phenyl ethyl alcohol. As ordinary commercial rose oil contains on the average not more than 1 per cent phenyl ethyl alcohol, it follows that in the production of Bulgarian rose oil about 2000 to 4000 kilos phenyl ethyl alcohol are absolutely wasted. We would mention in this connection that this result agrees in the main with that obtained by us in the summer of 1900<sup>2)</sup>. In order to ascertain the total oil-content of fresh rose blossoms, we extracted them with petroleum ether, and distilled the essential oil from the brown greasy extract with water vapour. The distillate of a milky cloudiness thus obtained

<sup>1)</sup> Berl. Berichte **34** (1901), 2803.

<sup>2)</sup> H. Walbaum. Über das Vorkommen von Phenyläthylalcohol in den Rosenblüthen; Berl. Ber. **33** (1900), 2306. See also our Report October 1900, 55.

was extracted with ether, and after evaporation of the ether yielded the pure essential oil which had been contained in the roses. The examination showed that this oil consisted for about 62 per cent of phenyl ethyl alcohol, boiling between 215 and 218°, identified by its phenyl urethane.

At that time we referred already to the remarkable difference between this oil and the ordinary oil obtained by distillation of the roses, and we submitted to ourselves the question whether this difference might only be due to the perhaps more rational process of production, or to new formation of phenyl ethyl alcohol?

We did not admit — as v. Soden and Rojahn maintain, — that this increased yield, which had also been observed in extracting withered rose leaves, could only be explained by an “evident” formation of phenyl ethyl alcohol. These authors agree with us, that such a formation of constituents of the oil by, possibly, decomposition of complex compounds after picking the blossoms is not a priori excluded, although such an occurrence particularly in roses has up to the present not been proved experimentally.

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E. J. Parry,<sup>1)</sup> opposes the view expressed by M. Holmes<sup>2)</sup> that Bulgarian rose oil for practical purposes could not be obtained pure. On the strength of more recent examinations of several samples from various districts in the Balkans, Parry has come to the conclusion that the adulteration of Turkish rose oil is not by any means so general as it is usually supposed to be. Without wishing to examine the opinions which have from time to time been expressed regarding the purity of Bulgarian rose oil, he considers it necessary to make a closer examination of one statement which has been made with authority, viz., the opinion, also mentioned in Gildemeister and Hoffmann's work on “The Volatile Oils”, that the Turkish rose oil found in commerce is mostly adulterated. The authors of that work base their statement chiefly on the great differences observed in the physical constants, and particularly in the stearoptene-content, of the ordinary commercial Bulgarian rose oil, and that obtained from the same rose, *Rosa damascena*, by Messrs Schimmel & Co., differences so enormous, that they cannot be accounted for by the mere difference in climate. The rose oils obtained at Miltitz, namely, showed throughout a higher stearoptene-content, 26 to 34 per cent, and consequently also a lower specific gravity, 0,845 to 0,855, at 30°, and a higher congealing point 27 to 37°, than all the commercial Bulgarian rose oils examined.

<sup>1)</sup> The Chemist and Druggist **60** (1902), 390.

<sup>2)</sup> Notes on pure Otto of Roses. Pharm. Journ. **67** (1901), 664.

whilst, on the other hand, Bulgarian rose oils which as particularly fine samples had been sent to exhibitions, showed an exceptionally near approach to the German oils in strength of odour and stearoptene-content.

This is not contradicted by the more recent investigations<sup>1)</sup> which, on the contrary, have confirmed those differences, and have added to them another observation, namely that the citronellol-content of the Turkish oil is also occasionally higher than that of the German product.

If Parry now has come to the conclusion that these differences carry no weight, and that the fact of a fairly extensive adulteration of Turkish rose oil cannot be deduced from them, we must say that we cannot agree with Parry's opinion. The possibility remains, that a part of the Bulgarian rose oils consists of a mixture of genuine oil of higher stearoptene-content, and geranium oils, whether saponified or only partly saponified, and it becomes a probability if the notorious trade in geranium oils in Turkey is taken into consideration. With regard to the difference between the oils of *Rosa centifolia* distilled in Germany, and those produced in France from the same rose, it may be allowed that this is due to climatic differences.

But it is at least doubtful whether this explanation is conclusive for the German and Turkish oils from *Rosa damascena*. Parry himself is unable to give any other proof of the purity of the samples examined by him, than the evidence that the oils obtained from various sources showed physical constants which agreed fairly well. He comes to the conclusion that the whole question of the adulteration of rose oils resolves itself of necessity principally into a question of price. Parry himself admits thereby that rose oil is an article of confidence, the value of which cannot yet be ascertained with certainty by chemical means.

Whether the differences in the oils obtained from the same rose in Germany and in Turkey are caused by climatic differences, or are due to adulteration of the Turkish oil, — in view of the uncertainty which still exists on the subject, one's opinion should be formed in accordance with the experience obtained.

**Rose Oil, German.** The stocks of our own distillate have all been sold, with the exception of some small quantities. Orders for delivery of the new season's product will receive every attention.

Here, as in Bulgaria, the development of the rose bushes has advanced much farther than in other years, in consequence of the mildness of the winter, and if no frost occurs, the gathering period will commence much earlier than usual.

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<sup>1)</sup> Report April 1901, p. 48.

**Rose Oil, Turkish.** The winter has been exceptionally mild in the Balkan districts. Lasting falls of snow have not occurred; the rose plants, which otherwise only shoot in April, showed already sprouts at the beginning of March, a time when frost and bad weather frequently occur, and when there is a considerable danger of the shrubs being killed by frost. But if the fine weather continues, the distillation will commence in good time, and the harvest will be a rich one. We must wait and see what will happen.

With regard to the much-discussed steps to be taken by the Bulgarian Government against the constantly increasing adulteration of rose oil, up to the present nothing has, unfortunately, taken place. The Bulgarian parliament has not enough stability to be able to carry through serious measures. The financial and economic conditions are too bad, to predict a prolonged existence for the present parliament, and if it is taken into consideration that in the last two years the Chamber has not even voted the budget, it is quite clear that no time can be found for matters of secondary importance.

For the present all remains therefore as of old.

As is shown by the following statistical table, the export of rose oil last year has fallen more than 50 per cent behind that of 1900:

### Export of rose oil.

Published by the Statistical Department.

Destination	From 1 <sup>st</sup> January to 31 <sup>st</sup> December			
	1901 Kilos	1900 Kilos	1899 Kilos	1898 Kilos
Austria-Hungary . . . . .	22	93	106	23
United Kingdom . . . . .	472	1174	633	707
Belgium . . . . .	4	—	3	6
Germany . . . . .	345	568	360	471
Greece . . . . .	—	0.375	—	0.005
Italy . . . . .	12	9	3	7
Russia . . . . .	119	202	155	134
United States . . . . .	760	849	716	380
Turkey (Constantinople) . .	564	886	522	872
France . . . . .	728	1548	1033	761
Holland . . . . .	—	6	2	4
Switzerland . . . . .	0.300	1	1	0.250
Norway . . . . .	0.250	—	—	—
Other countries . . . . .	1	10	—	65

Totals: 3027.550 5346.375 3534 3430.250

With regard to the progress of the new plantations of roses for the production of oil in Anatolia and the Caucasus, to which the newspapers have repeatedly referred during the last few years, we

find in the January number of the "Deutsches Handels-Archiv" II 67, the following official notice from the German Consulate General at Constantinople:

The rose cultivation in Anatolia, taken up during the last few years under the direction of a German export firm, has proved successful. But where no colonists from Eastern Roumelia are settled, there is unfortunately frequently a lack of sufficient experience and of rational treatment of the plants, and also of appliances for the distillation. The Caucasian rose oil has become a dangerous rival of the oil from Bulgaria and Eastern Roumelia. The roses recently planted in the Caucasus have given an uncommonly rich yield, and the quality of the oil is said to be even superior to the Bulgarian product.

In face of such reports, which appear over and over again, it is a curious fact that up to the present neither Anatolian nor Caucasian rose oil has been met with in commerce, and it may be concluded that the enterprise is still in the experimental stage. In view of the drop in the value, caused by over-production, and the competition into which our artificial rose oil enters with the natural product, a less opportune moment for the opening up of new sources of production could hardly have been selected.

**Oil of Rue.** As a continuation of their work on Algerian oil of rue, to which we referred in our last Report<sup>1)</sup>, H. v. Soden and K. Henle<sup>2)</sup> now publish the results of their examinations of methyl heptyl ketone. They identified it as normal methyl heptyl ketone by oxidation into normal caprylic acid (with bromine and potash solution), production of caprylic acid amide of the melting point 105 to 106°, and conversion of the methyl heptyl ketoxime (b. p. 108—109° at 6 mm pressure) into normal heptylamine of the boiling point 153—156° (according to Beckmann-Wallach's method). Algerian oil of rue, as distinct from ordinary rue oil, contains about twice as much methyl heptyl ketone as methyl nonyl ketone. The total content of the two ketones amounts to about 90 per cent. Methyl heptyl ketone has a distinctly more powerful and aromatic odour than methyl nonyl ketone, and this accounts for the difference in the odour between Algerian and ordinary rue oils. In addition to these two ketones, fairly considerable quantities of esters are present in Algerian oil of rue, — probably acetic esters of the secondary alcohols corresponding to the ketones.

Algerian rue oil also shows a faint blue fluorescence.

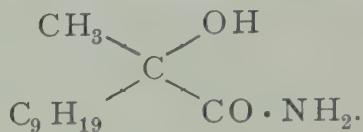
H. Carette<sup>3)</sup> has recently prepared derivatives of methyl nonyl ketone. According to his observations hydrocyanic acid reacts with

<sup>1)</sup> Report, October 1901, p. 47.

<sup>2)</sup> Pharm. Zeitung 46 (1901), 1026.

<sup>3)</sup> Compt. rend. 134 (1902), 477.

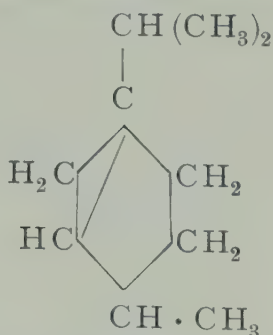
methyl nonyl ketone only when a few drops of concentrated ammonia liquor are added. The product of reaction is a brown oil which very readily becomes decomposed, and which cannot be distilled without strong decomposition, even at greatly reduced pressure. When heated with concentrated hydrochloric acid, it yields a crystalline product of the melting point  $86^{\circ}$  to  $87^{\circ}$ , methyl nonyl glycollic acid amide:



From the presence of this body it must be concluded that the first-named product represents the corresponding nitrile. If this nitrile is treated for some time with strong acid at the temperature of the water bath, two reaction-products are formed, of the melting points  $46^{\circ}$  and  $185^{\circ}$ . Carette recognised the former as methyl nonyl oxyacetic acid; the second is no doubt methyl nonyl amidoacetic acid. Further examinations of these products are in progress.

**Oil of Sage.** On fractionating German oil of sage H. Seyler<sup>1)</sup> obtained 1 to 2 per cent of a first fraction boiling below  $155^{\circ}$ , which could be separated into three portions by repeated distillation over sodium. The fraction first passing over, of the boiling point  $142-145^{\circ}$  ( $d_{20}^{\circ} = 0.80$ ;  $n_D = 1.4438$ ;  $\alpha_D = +1^{\circ}40'$ ) gave analyses corresponding to  $\text{C}_{10}\text{H}_{18}$ . This hydrocarbon, called "salvene", when oxidised with potassium permanganate, yielded almost quantitatively an acid, whose semicarbazone  $\text{C}_{10}\text{H}_{16}\text{O}_2\text{CON}_3\text{H}_3$  melted at  $204^{\circ}$ , and which possibly is identical with  $\beta$ -tanacetoketonic acid ( $\beta$ -thujaketonic acid).

Salvene has probably the following constitutional formula:



From the first runnings of a Spanish oil of sage no salvene could be isolated.

**Sandalwood Oil (East Indian).** At the Government auctions of wood in India, which took place some few months ago, a compara-

<sup>1)</sup> Berl. Berichte **35** (1902), 550.

tively large quantity was offered, viz., about 2215 tons, as compared with about 1700 tons in the previous year. The expected rise in the prices has for this reason not taken place, but on the other hand there has neither been a fall, so that the values remain approximately the same as in the previous year. No information is given whether a considerable proportion of the quantities offered has remained unsold, but we are inclined to believe that such has been the case, for the consumption of this article, which belongs to the fashionable drugs, has probably not entirely escaped the effects of the general depression of trade.

The following table gives further particulars of the quantities sold in the various districts:

District	Koti	Date	Quantity
Shimoga	Tirthahalli	18 <sup>th</sup> Nov. 1901	about 150 tons
"	Sagar	22 <sup>nd</sup> " "	" 220 "
"	Shimoga	27 <sup>th</sup> " "	" 400 "
Kadun	Chikmagalur	2 <sup>nd</sup> Dec. "	" 160 "
Hassan	Hassan	6 <sup>th</sup> " "	" 250 "
Bangalore	Bangalore	10 <sup>th</sup> " "	" 120 "
Mysore	Seringapatam	13 <sup>th</sup> " "	" 325 "
"	Hunsur	16 <sup>th</sup> " "	" 375 "
Fraserpett	Fraserpett	19 <sup>th</sup> " "	" 215 "

Total about 2215 tons

The competition of the numerous manufacturers of sandalwood oil has in recent years become keener than ever; as a consequence, every possible advantage must be taken, both in purchasing the wood and in the manufacture of the oil. With reference to the former, we have made arrangements with a firm of Indian commission agents who make a speciality of this trade, by which we buy at the auction prices, with a moderate commission added. For the manufacture of oil from the wood we have in our new factory laid down plant which we believe is unique, and which enables us to produce daily up to 4 cwts. of sandalwood oil. With regard to the quality of our sandalwood oil, we consider it hardly necessary to say another word. It is a well-known fact that the methods which are nowadays employed for testing the quality, have been devised by us.

Some sample lots of sandalwood from New Caledonia and Western Australia (Swan River) are at this moment on the way for us. We will refer to these again in our next Report.

▶ **Snake-root Oil (Canadian).** The essential oil distilled from the underground portions of *Asarum canadense* has been examined years ago by Fr. B. Power. The progress made, not only in the knowledge of the constituents of essential oils, but also with regard to

the methods of examination, has induced Power, jointly with Fr. B. Lees, to submit the oil to a further careful examination<sup>1)</sup>.

According to this the composition of the oil is after all somewhat more complicated than the previous examination would lead one to believe. The authors, namely, recently found the following constituents: 1. a phenol  $C_9H_{12}O_2$ ; 2. pinene, clearly as a mixture of the two optically active modifications; 3. d-linalol; 4. l-borneol; 5. l-terpineol; 6. geraniol; 7. eugenol methyl ether; 8. a blue oil of indefinite composition, consisting of oxygenated compounds of alcoholic character; 9. a lactone  $C_{14}H_{20}O_2$ ; 10. palmitic acid; 11. acetic acid, and 12. a mixture of higher and lower fatty acids.

The content of eugenol methyl ether in the original oil, ascertained by Zeisel's method, amounts to 36.9 per cent, the ester-content (calculated as  $C_2H_3O_2 \cdot C_{10}H_{17}$ ) to 27.5 per cent. The total content of alcohols  $C_{10}H_{18}O$  was found to be 34.9 per cent, from which it follows that about 13.3 per cent alcohols are present in the non-esterified state. As the oil also contains about 2 per cent of pinene, the high-boiling constituents, the blue oil, etc., would represent a little less than 20 per cent.

**Spearmint Oil.** The prices of fine American distillates have increased considerably, in sympathy with those of peppermint oil. The stocks in America are unimportant. In Thuringia the distillation of this article has practically ceased.

**Star-anise Oil.** Business in this East-Asiatic staple article has been so slow during the last six months, that the depressed quotations could not recover. The sale of Chinese oil meets with strong competition from the Tonquinese product, which is of superior quality; only in England and in some oriental countries certain Chinese brands are still blindly preferred. And yet it will be remembered that it was the Tonquin oil which had a salutary effect on the Chinese product when the quality of the latter began to deteriorate, and which prevented the adulteration from increasing in volume. The market quotations fluctuate between 4/6 and 4/7. It is said that at the end of January compulsory sales under hand have taken place at London at even less than 4/.

Prices were lately a little firmer, in consequence of a cablegram according to which large quantities of staranise oil have been burnt in China.

In our Reports of April and October 1898 we have already mentioned in detail the advantages of the Tonquin oil, and we wish all the more to call attention to what we then said, as at the present

<sup>1)</sup> Journal of the chem. Soc. 81 (1902), 59.

time attempts are made to throw discredit on the Tonquin oil by quoting it at lower prices than the Chinese brands.

In the case of star-anise oil it is not a question of the brand, but of the anethol content, which is expressed by the congealing point. For Chinese oil the latter is generally guaranteed as  $15^{\circ}$ , whilst Tonquin oil mostly shows 16 to  $17^{\circ}$ , and at equal prices should absolutely be preferred.

**Thyme Oil.** Contrary to the usual observations that French thyme oil as a rule has a phenol-content of 20 to 25 per cent, which but rarely increases up to 42 per cent, Jeancard and Satie<sup>1)</sup> report that according to their experience the phenol-content varies between 5 and 60 per cent, and that the figures mentioned above can only be taken as average values. Jeancard and Satie have proved by experiments that the phenol-content is most intimately connected with the method of distillation. As, namely, in steam distillation the phenols only pass over more abundantly towards the end of the process, a smaller or larger phenol-content of the oil obtained from the same material will entirely depend upon the manner in which the distillation has been conducted.

Both specific gravity and solubility in dilute alcohol (70 per cent by volume) increase with the phenol-content, the former by about 0.0013 to 0.0015 for each per cent phenol.

We would here observe that the authors have partly had to do with oils which were not normal distillates, but rather individual fractions of one distillation. According to our experience French thyme oils have always the phenol-content of about 20 per cent mentioned above.

**Vetiver Oil.** We have recently completed the manufacture of a large parcel of our own incomparable distillate. This is of quite exceptional richness, and is more economical in use than the cheap competition products. We can strongly recommend it.

**Wintergreen Oil.** L. Portes and A. Desmoulières<sup>2)</sup> have found that in strawberries a body is present, which gives a violet colour-reaction with very dilute solution of ferric chloride. Their experiments, made with a large number of different varieties of strawberries, prove that this substance is salicylic acid. Whether the acid, as is supposed, is present in the fruit in the form of its methyl ester, a question to be decided by the further experiments which the authors have in view.

<sup>1)</sup> Bull. soc chim. III. 25 (1901), 893.

<sup>2)</sup> Journ. de pharm. et de chim. VI. 14 (1901), 342.

**Wormwood Oil.** This article is at present scarce and difficult to obtain in good qualities. The stocks of American oil are practically exhausted, and cannot be supplemented until next autumn. It is to be hoped that the high prices have led to a resumption of the cultivation on a large scale. In France it has been reduced to the lowest limits, in consequence of the regulations of the well-known Act of 29<sup>th</sup> December 1900 relating to the sale of spirits; for this reason no important supplies must be expected from that country, unless the orders are placed in advance. Under these circumstances the only thing to be done is, to take up the cultivation of wormwood ourselves, — a task which will receive further consideration in the course of this summer. The cultivation requires much care and suitable fertilisation. How much it is possible to obtain by these means is shown clearly by a product we have before us, for which the herb is grown in the immediate vicinity of Paris. This quality puts all others in the shade.

**Ylang-Ylang Oil, artificial, "Schimmel & Co."** The great improvement made in our product by our most recent discoveries is acknowledged on all sides. It requires indeed an expert knowledge to detect any difference between this product and the best brands of imported oil. In working up, the oil also answers admirably, as we have ascertained ourselves, and has been confirmed from many quarters. The odour is flowery and fragrant, and is durable in the manufactured product. The oil decidedly merits the greatest attention from the perfumery trade. We are certain that it will everywhere be a credit to us, and we ask our clients to treat it with full confidence.

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Our notes on ylang-ylang oil which appeared in our last Report, have induced Georges Darzens<sup>1)</sup> to publish also some results which he had already obtained some time ago in examining this oil in the laboratory of the firm L. T. Piver & Co. Darzens saponified 250 grammes ylang-ylang oil, which had previously been washed with distilled water, with aqueous potash liquor, heating the mixture for ten hours to 100°. On distilling the aqueous liquor, methyl alcohol passed over, which was subsequently converted, for further identification, into benzoic acid ester with its characteristic odour. The phenols were then separated from the liquor by the introduction of carbonic acid, and shaken with benzoyl chloride and soda liquor. This produced the benzoyl compound of p-cresols melting at 70 to 71°. Acetic and benzoic acids were detected in

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<sup>1)</sup> Bull. soc. chim. III. 27 (1902), 83.

the saponification liquor. The author is of opinion that p-cresol is present in ylang-ylang oil in the form of acetyl-p-cresol, which compound is said to possess an ylang-like odour.

As we mentioned already in our previous Report, we have also been able to detect methyl alcohol in ylang-ylang oil; this is not present in the free state, but in the form of ester, for it was produced in saponifying, with aqueous potash liquor, the ester fractions of the oil boiling at 10 mm pressure between 82 and 120°. The methyl alcohol obtained from these fractions after saponification of the latter, was for further identification converted with phosphorus and iodine into methyl iodide. In the saponification liquor benzoic acid of the melting point 122° could be detected. These experiments show that methyl alcohol was present in the above fractions combined with benzoic acid as methyl ester of benzoic acid, a fact which is confirmed by the odour. The benzoic acid of ylang-ylang oil, however, is also present in this oil combined with benzyl alcohol. This result was obtained in rectifying a fairly large quantity of the oil with water vapour, when a residue remained which passed over with difficulty, and which on saponification split up into benzoic acid and benzyl alcohol. The latter was further identified by its constants, and by conversion into benzaldehyde and the phenyl urethane melting at 78°.

Benzyl alcohol could also be detected, by oxidation into benzaldehyde, in fractions which according to their boiling points could contain benzyl alcohol or benzyl acetate, but no benzyl benzoate<sup>1)</sup>. A further point in favour of the presence of free benzyl alcohol in ylang-ylang oil is the detection of this alcohol, by v. Soden and Rojahn<sup>2)</sup>, in a distillation water of ylang-ylang oil obtained from Manila.

**Ylang-ylang oil, genuine, "Sartorius brand".** The present state of affairs in and around Manila, although fairly normal, is not yet such that a reduction in the purchase prices of flowers could have been enforced. The demand for the fine qualities of oil has risen so considerably, that hardly enough material can be procured, and so long as this condition lasts the value must remain high.

The owners of the justly preferred brand "Sartorius" have lately succeeded, with great exertions, and by means of improved apparatus, to overcome the demand, so that we were able to meet in full the requirements of our regular clients. If occasionally slight delays have taken place, it is a matter which, in view of the enormous distance, cannot be helped.

<sup>1)</sup> These results were obtained during an examination of ylang-ylang oil, brand "Sartorius", made in the year 1895.

<sup>2)</sup> Berl. Berichte 34(1901), 2809.

The quality of the various deliveries was throughout of equal excellence. We would request early notice of the quantities required, when everything possible will be done with regard to delivery.

The "Chemist and Druggist" of 8<sup>th</sup> March No. 1154, contains an interesting article on ylang-ylang oil, which we reproduce here:

The acquisition of the Phillippine Islands by the United States of America has naturally led the Government to investigate the condition of various industries carried on in the archipelago, with the idea of ultimately concentrating the trade into American channels. The distillation of essential oils, which has flourished from time immemorial in the Phillippines, was one of the first to attract attention, and at the instance of several American houses, an official report on the ylang-ylang oil industry has been compiled. Hitherto supplies for the United States have come through Germany and France, those countries having had practically a monopoly of the trade, but no doubt the Americans will now make an effort to obtain supplies direct. It may be a difficult matter, as the distillation of the oil is principally done by Germans, and the bulk of the output is contracted for by German houses. Indeed, the industry was first conducted by Germans in the island of Luzon in the early sixties of last century, but it was not until 1878, when it was first exhibited at Paris, that the oil became widely known. The ylang-ylang tree (*Cananga odorata* Hooker, or *Unona odoratissima*), common to many localities south of Manila, is found chiefly in the well-populated provinces, where it thrives best. It is propagated by planting seedlings or cuttings about twenty feet apart each way, when they grow rapidly in almost any soil. The first flowers appear in the third year and in the eighth year. A tree yields as high as 100 lbs. The blossom grows in every month of the year, but the greatest yield is from July to December. The petals are subjected to the simplest form of distillation, and the best quality of oil is as clear as distilled water and fragrant, while the second quality is yellowish and somewhat empyreumatic. About 75 lbs. of flowers yield 1 lb. of oil; flowers are worth from 8 c. to 15 c. gold per lb., and the cost of manufacturing is about \$ 4 per lb. There are flowering groves in many parts of South Luzon and the Visayan Islands, but the vicinity of Manila is also well adapted to the growth of this tree. Naturally the Spanish-American war greatly interfered with the industry, but as affairs have been practically settled for some months past, we understand that distillation has been taken up on the same scale as before. Last year there was a great scarcity of fine ylang-ylang oil on the European markets, with an abundance of medium and cheaper qualities. There is little sale for the oil on this market, but occasionally direct shipments of small quantities from Manila are sent to London and offered in public auction. Although Java produces ylang-ylang oil in small quantities, it has not the commercial importance of Manila oil, which is much sought after by soap-makers and perfumers.

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### The New Swedish Pharmacopœia.

The Swedish Pharmacopœia (Pharmacopœia svecica ed. VIII) which has come into force on January 1<sup>st</sup> 1902, is the subject of a general review by G. Frerichs in the *Apotheker-Zeitung*.<sup>1)</sup> In this review

<sup>1)</sup> Vol. 16 (1901), 837 and 845.

it is in the first place acknowledged that in the new edition "in accordance with the present-day position of science, much greater value is attached to the test of medicaments than used to be the case". The same opinion applies to the essential oils mentioned in that pharmacopœia, and, although on the whole it gives the same regulations as the German Pharmacopœia, it goes in some cases even a little farther with regard to the requirements. This is, for example, apparent, by the endeavours made to substitute, wherever possible, the active constituent of an essential oil for the oil itself. In addition to the preparations anethol, carvone, and eugenol, which have been included in the German Pharmacopœia, the Swedish authority substitutes also the use of cinnamic aldehyde in place of cassia oil, and of eucalyptol instead of cajeput and eucalyptus oils. The Swedish Pharmacopœia also takes into consideration the optical activity, which, as is well-known, is a factor of decided importance in judging an oil, and which unfortunately is still passed over in silence by the German Pharmacopœia. Matters of an apparently subordinate character are also duly considered in the Swedish Pharmacopœia; thus, it gives an exact definition of the term "weighable residue", etc.

On one point, however, we have looked in vain for information, both in the Swedish and the German Pharmacopœia, namely at what pressure are the boiling points taken? This factor appears to us of too much importance, not to call special attention to it, and it might be recommended to include in the pharmacopœias in future exact directions on this point also. We suppose, that the boiling points are taken at the normal barometric pressure of 760 mm. We would seize this opportunity to point out that in determining the boiling point, the whole mercury thread should be surrounded by the vapour of the liquid, a matter which can be attained by the use of shortened normal thermometers. Otherwise the necessary corrections must be made, in order to avoid totally incorrect results.

It appeared to us that for the purpose of a better survey of the individual points discussed, a tabulated statement would be found useful; we therefore give such a statement in the following pages, in which we have placed for each oil the German requirements against those of the Swedish Pharmacopœia.

The following general notes are added as preliminary remarks:

$d_{15^{\circ}}$  means the specific gravity at  $15^{\circ}\text{C.}$ ,

$\alpha_D$  means the optical rotation in a tube of 100 mm length.

The temperature of the solutions is in all cases  $20^{\circ}\text{C.}$

"Parts" means parts by weight.

The strengths of alcohol are:

I. In the Swedish Pharmacopœia:

- a) *Spiritus* contains 90.3 to 91 per cent alcohol by volume,
- b) *Spiritus dilutus* contains 63.8 to 64.8 per cent alcohol by volume,
- c) *Spiritus tenuis* contains 48.4 to 50.6 per cent alcohol by volume.

A mixture of 1 part *Spiritus* and 4 parts *Spir. dil.* has an alcohol-content of about 69 to 70 per cent by volume.

II. In the German Pharmacopœia:

- a) *Spiritus* contains 90 to 91.2 per cent alcohol by volume,
- b) *Spiritus dilutus* contains 69 to 69 per cent alcohol by volume.

Swedish Pharmacopœia.

German Pharmacopœia.

**Anethol.**

$d_{25}^{\circ} = 0.984-0.986.$

$d_{25}^{\circ} = 0.984-0.986.$

$\alpha_D = \pm 0^{\circ}.$

Melting point:  $20-21^{\circ}.$

Melting point:  $20-21^{\circ}.$

Boiling point:  $233-234^{\circ}.$

Boiling point:  $232-234^{\circ}.$

Soluble in less than 2 parts of

Soluble in 2 parts *Spiritus*.

*Spir.*,<sup>1)</sup> neutral reaction of the solution.

**Carvone.**

$d_{15}^{\circ} = 0.963-0.966.$

$d_{15}^{\circ}$  not below 0.960.

$\alpha_D =$  to the right.

Boiling point:  $229-230^{\circ}.$

Boiling point:  $229-230^{\circ}.$

Soluble in *Spir.* in every proportion.

Soluble in 2 parts *Spir. dil.*

Soluble in 20 parts *Spir. ten.*

A mixture of 1 cc each carvone and *Spiritus*, must remain unchanged on the addition of one drop of dilute solution of ferric chloride, or at most show a faint reddish violet tinge.

**Cinnamic aldehyde.**

$d_{15}^{\circ} = 1.054-1.056.$

$\alpha_D = \pm 0^{\circ}.$

The German Pharmacopœia does not mention the pure aldehyde, but cassia oil:

Boiling point at about  $252^{\circ}$ , with partial decomposition.

<sup>1)</sup> In testing the solubility, particular attention should in this case be paid to the temperature, as otherwise incorrect conclusions would be arrived at.

## Swedish Pharmacopœia.

## German Pharmacopœia.

Soluble in *Spiritus* in every proportion.

Cinnamic aldehyde should solidify when the temperature is much reduced, and should melt again at  $7.5^{\circ}$ .<sup>1)</sup> If a few drops of cinnamic aldehyde are mixed, whilst being cooled, with an equal number of drops of fuming nitric acid, the whole liquid congeals into a yellow crystalline mass, which dissolves in water under separation of yellow drops of oil.

Cinnamic aldehyde, as an aldehyde, separates metallic silver, and when heated is soluble in a solution of sodium bisulphite. The spirituous solution (1 + 50) should not be changed by one drop of ferric chloride solution.

Cinnamic aldehyde should give no chlorine reaction.

**Eucalyptol.**

$$d_{15^{\circ}} = 0.928 - 0.930.$$

$$\alpha_D = \pm 0^{\circ}.$$

Boiling point:  $176 - 177^{\circ}$ .

Soluble in *Spiritus* in every proportion. When reduced considerably in temperature, eucalyptol should congeal to a crystalline mass which again melts at  $-1^{\circ}$ .<sup>2)</sup>

If some bromine vapour is introduced in a test tube of which the interior walls have been moistened with one or two drops

<sup>1)</sup> The melting point lies not at  $+7.5^{\circ}$ , but at  $-7.5^{\circ}$ .

<sup>2)</sup> The absence of congelation is not always a sign of a faulty preparation, as eucalyptol can often be cooled fairly much below the solidifying point without congealing; in such cases it is sufficient to add a small crystal of solid eucalyptol, when the whole mass will soon congeal.

## Swedish Pharmacopœia.

## German Pharmacopœia.

of eucalyptol, numerous crystals of a faint yellow colour should appear on the inside of the tube.

**Eugenol.**

$$d_{15^{\circ}} = 1.072 - 1.074^1).$$

$$\alpha_D = \pm 0^{\circ}.$$

Boiling point:  $251-253^{\circ}$ .

Soluble in *Spiritus* and ether in every proportion.

Soluble in 2 vol. *Spir. dil.*

The strongly diluted spirituous solution is coloured blue with ferric chloride.

A mixture of eugenol and soda solution (25% NaOH) in equal volumes congeals to a solid crystalline mass.

$$d_{15^{\circ}} = 1.072 - 1.074.$$

Boiling point:  $251-253^{\circ}$ .

Dissolves with difficulty in water, readily in alcohol, ether and glacial acetic acid.

Soluble in 2 vol. *Spir. dil.*

When mixing 1 gramme eugenol with 26 cc water and 4 cc soda solution (about 15% NaOH) a clear liquid is formed, which readily becomes cloudy when exposed to the air.

**Fennel Oil.**

$$d_{15^{\circ}} = 0.965 - 0.975.$$

$$\alpha_D = + 12^{\circ} \text{ to } + 24^{\circ}.$$

Solidifies when temperature much reduced.

$$d_{15^{\circ}} = 0.965 - 0.975.$$

When fennel oil is cooled to below  $0^{\circ}$ , crystals of anethol separate out, which only dissolve again upon warming to  $+ 5^{\circ}$ .

<sup>1)</sup> We have recently taken up the distillation of eugenol in vacuo, and thereby supply an absolutely anhydrous preparation. The remarkable occurrence has hereby been noticed that the eugenol becomes a little lighter ( $d_{15^{\circ}} = 1.0716$ ), but again increases in specific gravity ( $d_{15^{\circ}} = 1.0725$ ) when shaken up with water. This is probably due to an addition of water to the unsaturated side chain, as we have observed a similar occurrence also with other compounds having an unsaturated side chain.

We would further take the opportunity to point out that with the Westphal balance frequently used by chemists, it is not always possible to determine with exactitude the third decimal; in these balances an unequal division of temperature easily occurs, as the liquid cannot be kept constantly moving, in consequence of which the thermometer, which serves at the same time as the sinking body, does not always indicate the exact average temperature of the whole liquid.

## Swedish Pharmacopoeia.

## German Pharmacopoeia.

Soluble in 1—2 parts *Spiritus*.Soluble in equal volume of *Spiritus*.

The spirituous solution (1+2) should not be coloured by one drop of ferric chloride-solution.

**Lavender Oil.** $d_{15^{\circ}} = 0.885—0.895$ . $d_{15^{\circ}} = 0.885—0.895$ . $\alpha_D =$  slightly lævogyre.Soluble in *Spiritus* in every proportion.Soluble in 3 parts *Spir. dil.*<sup>1)</sup>

Saponification number not below 90, corresponding to a minimum ester-content of 31.5 per cent.

Saponification number not below 84, corresponding to a minimum ester-content of 29.4 per cent.

**Lemon Oil.** $d_{15^{\circ}} = 0.855—0.861$ . $d_{15^{\circ}} = 0.858—0.861$ . $\alpha_D = +60^{\circ}$  to  $+65^{\circ}$ .<sup>2)</sup>

With 5 parts *Spiritus*, lemon oil should make a solution which as a rule is not completely clear.

Lemon oil may only have an unimportant precipitate; it must not show a strongly acid reaction, and when diluted as directed it should have a fine pure odour of lemons.

**Mace Oil.**<sup>3)</sup> $d_{15^{\circ}} = 0.855—0.930$ . $d_{15^{\circ}} = 0.890—0.930$ . $\alpha_D =$  dextrogyre.Soluble in 3 parts *Spiritus*.Soluble in 3 parts *Spiritus*.

<sup>1)</sup> Compare our previous Report, p. 35.

<sup>2)</sup> With regard to the optical rotation, the lower limit of  $60^{\circ}$  should be reduced to  $58^{\circ}$ , as such rotation is frequently observed with pure oils. It should moreover be taken into consideration that the rotatory power of lemon oil varies considerably with the temperature; the above figures refer to a temperature of  $20^{\circ}$ , and it is advisable to conduct the observations at that temperature.

<sup>3)</sup> It should be noted that in the Swedish Pharmacopoeia the name "mace oil" is given to oil of mace, whilst in the German Pharmacopoeia this name applies to oil of nutmeg. The difference between the two oils is small, but yet it is there. The limits between which the specific gravity is allowed to fluctuate, would appear to us somewhat wide in the Swedish Pharmacopoeia.

**Mustard Oil.**

$$d_{15}^{\circ} = 1.016 - 1.025.$$

Soluble in every proportion in *Spiritus*, ether, benzene and carbon disulphide.

If 1 part mustard oil, 1 part *Spiritus*, and 2 parts ammonia liquor are heated to about  $50^{\circ}$ , the liquid, which has at first become cloudy through the separation of drops of oil, should become clear, and after cooling, colourless crystals with an odour like leeks should gradually separate out.

On distillation the bulk of mustard oil should pass over between  $147$  and  $152^{\circ}$ , and neither the first nor the last portion of the distillate should have a specific gravity differing in a marked degree from that of mustard oil itself.

If 2 to 4 cc concentrated sulphuric acid are slowly added to 1 cc mustard oil, while being well cooled, a perfectly clear, yellow liquid should be formed, which is free from the pungent odour of mustard oil.

5 cc of a spirituous solution (1 + 5) should not be changed by one or two drops of a solution of ferric chloride.

**Determination of the sulphur-content.**

5 grammes mustard - spirit (1 + 49) are mixed in a measuring flask of 100 cc capacity with

$$d_{15}^{\circ} = 1.018 - 1.025.$$

Soluble in *Spiritus* in every proportion.

Boiling point:  $148 - 152^{\circ}$ .

If 6 grammes sulphuric acid are gradually added to 3 grammes mustard oil, while being well cooled, the mixture, when shaken up, will evolve gas. The yellow mixture, which in no case should have a dark colour, is at first perfectly clear, then becomes viscous, and occasionally crystalline, whilst the pungent odour of mustard oil disappears.

Mustard oil diluted with 5 parts *Spiritus* by volume, should not be changed when a solution of ferric chloride is added in drops.

5 cc of a solution of mustard oil in alcohol (1 = 50) are mixed in a 100 cc measuring flask with

## Swedish Pharmacopœia.

## German Pharmacopœia.

50 cc of  $\frac{n}{10}$  silver nitrate and 2 cc ammonia liquor; the flask is well stoppered and set aside, being meanwhile frequently shaken up. After 24 hours, 5 cc nitric acid and 1 cc solution of iron alum are added, the liquid diluted with water up to the 100 cc mark, shaken up, and filtered through a dry filter. 50 cc of the filtrate should not require less than 14.9 nor more than 16.7 cc of  $\frac{n}{10}$  ammonium sulphocyanate.

50 cc  $\frac{n}{10}$  silver nitrate and 10 cc ammonia liquor; the flask is well stoppered and set aside for 24 hours, being meanwhile frequently shaken up. After diluting the liquid up to the 100 cc mark, 50 cc of the clear filtrate, after the addition of 6 cc nitric acid and 1 cc solution of ferric ammonium sulphate, should require 16.6 to 17.2 cc of  $\frac{n}{10}$  ammonium sulphocyanate to produce a red colour.

**Peppermint Oil.**

$$d_{15^{\circ}} = 0.900 - 0.920.$$

$$a_D = \text{lævogyre.}$$

Soluble in 3 to 4 parts of a mixture consisting of 1 part *Spiritus* and 4 parts *Spir. dil.* clear, or at most with opalescence.

If a little iodine is moistened with a few drops of peppermint oil, no detonation should occur.

$$d_{15^{\circ}} = 0.900 - 0.910.$$

Soluble in 4 to 5 parts *Spir. dil.*

**Rosemary Oil.**

$$d_{15^{\circ}} = 0.890 - 0.910.$$

$$a_D = \text{dextrogyre.}$$

Soluble in *Spiritus* in every proportion.<sup>1)</sup>

$$d_{15^{\circ}} \text{ not below } 0.900.$$

Soluble in one half part *Spiritus*.

**Sandalwood Oil.**

$$d_{15^{\circ}} = 0.970 - 0.985.$$

$$a_D = \text{slightly lævogyre}^2).$$

Soluble in *Spiritus* in every proportion.

$$d_{15^{\circ}} = 0.975 - 0.985.$$

Soluble in 5 parts *Spir. dil.*<sup>3).</sup>

<sup>1)</sup> A turbidity which generally occurs at the commencement of the addition of alcohol originates from the presence of water in the oil, as thereby the small quantity of alcohol is so much diluted, that it is unable to make a clear solution in the rosemary oil. An oil dehydrated with anhydrous sodium sulphate does not show this passing turbidity.

<sup>2)</sup> The lævogyrations may nevertheless be from  $-17^{\circ}$  to  $-20^{\circ}$ .

<sup>3)</sup> Compare our previous Report, p. 49.

Swedish Pharmacopoeia.

German Pharmacopoeia.

Soluble in 5 to 6 parts of a mixture consisting of 1 part *Spiritus* and 4 parts *Spir. dil.*

Slightly acid reaction.

Slightly acid reaction.

**Turpentine Oil (crude).**

$d_{15^{\circ}} = 0.855-0.875^1$ .

Boiling point:  $150-162^{\circ}$ .

Turpentine oil should have no empyreumatic odour.

$d_{15^{\circ}} = 0.865-875$ .

Boiling point: mainly  $155-162^{\circ}$ .

Soluble in 12 parts *Spiritus*.

**Turpentine Oil (rectified).**

$d_{15^{\circ}} = 0.860-0.870$ .

Boiling point:  $155-162^{\circ}$ .

Soluble in 10 to 12 parts *Spiritus*.

When shaken up with an equal quantity of water, the oil of turpentine should impart no acid reaction to the former. When evaporated on a water bath only traces of a solid residue may remain.

$d_{15^{\circ}} = 0.860-0.870$ .

Boiling point: mainly  $155-162^{\circ}$ .

Colourless, neutral liquid.

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**The French Pharmacopœia.**

In the French Pharmacopœia at present in force the particulars about essential oils leave very much to be desired, and it should therefore be welcomed that the Pharmacopœia Committee, on the occasion of the issue of a new pharmacopœia, will remedy this matter thoroughly by omitting the superfluous details about the production of the oils, and substituting instead directions regarding the properties of the oils and tests as to their purity.

In connection with a discussion of the proposals made by the Pharmacopœia Committee, Bourquelot makes some observations,<sup>2</sup> also respecting essential oils, from which we abstract the following:

In order to avoid repetitions, it is desirable that in the first place under a special heading "*Essences en général*", directions are given

<sup>1</sup>) We consider the requirement of the German Pharmacopœia, of a specific gravity for oil of turpentine of 0.865 to 0.875, as more correct. This naturally accounts for the difference in the boiling point.

<sup>2</sup>) Journ. de pharm. et de chim. VI. 14 (1901), 563.

for the detection of the most common adulterants (alcohol and fatty oils), and that the individual oils should then follow. Of these, Bourquelot only mentions for the present the following:

**Oil of Bergamot.** The following requirements are proposed: The oil should contain at least 35 per cent linalyl acetate<sup>1)</sup> and when evaporated on a water bath, should leave a residue of not more than 6 per cent.

**Oil of Bitter Almonds.** The oil should contain hydrocyanic acid, and have a neutral or an acid reaction. It should further be tested for adulteration with nitrobenzene.

**Oil of Cloves.** Several identification reactions are proposed, moreover one test each for the absence of phenol, and the absence of petroleum, fatty oils and oil of turpentine.

**Oil of Lemon.** Here the optical behaviour should be considered in the first instance. At 15 to 20° the oil should have a rotatory power of  $+57^\circ$  to  $+67^\circ$ ,<sup>2)</sup> and for the first 10 per cent of the distillate the rotation should at most be 5° lower than that of the original oil.

A continuation of Bourquelot's work has unfortunately not yet appeared, so that at present the discussion is limited to these few oils. In due course we propose to return to the subject.

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## Novelties.

We are again indebted to the courtesy of various patrons and friends of our firm, for samples of a number of essential oils which had not hitherto been prepared. As in most instances the samples were only small, we have had to limit ourselves to the determination of the general properties of the various oils, of which we give results below.

Mr. Stavenhagen of Reggio (Calabria) sent us an oil which had been obtained from the flowering herb of *Artemisia variabilis* Ten. It has a brown colour, and an odour reminding of petitgrain oil. The specific gravity at 15° was 0.9115, the optical rotation  $-9^\circ 20'$ . Free acid is present only in insignificant quantity (acid number 1.7),

<sup>1)</sup> For these determinations the Pharmacopœia Committee proposes the use of normal solutions. For the purpose of greater exactness it may be recommended to follow the example of other pharmacopœias, and prescribe semi-normal solutions.

<sup>2)</sup> 67° appears to us very high, even for a temperature of 15°. As the rotation of lemon oil varies considerably with fluctuations in the temperature, we would consider it more appropriate to fix the same at a definite temperature, and, for example, require a rotatory power of  $+58^\circ$  to  $+65^\circ$  at 20°.

and the content of both ester and alcohol is also small (saponification number 15.5; sapon. number after acetylation 49.1). The oil is only incompletely soluble in alcohol; even when absolute alcohol is used, the liquid, at first clear, becomes cloudy after adding 10 to 12 volumes. From this it might be concluded that we have to deal with an oil rich in terpenes or sesquiterpenes. In our next Report we hope to give further details on this subject.

From Mr. Henry Azgour of Jaffa we received the following oils, which had been obtained from plants growing wild in the Jordan valley:

1. **Anise Oil.** Spec. grav. ( $15^{\circ}$ ) 0.9609; optical rotation  $+35^{\circ}29'$ . The oil is readily soluble in 90 per cent alcohol. It appears to contain only very little anethol, as it does not congeal even when cooled to as low as  $-15^{\circ}$ . It is probably a kind of fennel oil.

2. **Oil of Laurel leaves.** Spec. grav. ( $15^{\circ}$ ) 0.9237; optical rotation  $-15^{\circ}34'$ . Soluble in 1 volume and more of 80 per cent alcohol.

3. **Oil of Myrtle.** Spec. grav. at  $15^{\circ} = 0.9113$ ; opt. rot.  $+13^{\circ}40'$ . Soluble in 0.8 volume and more of 80 per cent alcohol. Acid number 5.15; saponification number 29.2.

The oils of both laurel leaves and myrtle correspond to the ordinary distillates.

4. **Peppermint Oil.** Spec. grav. at  $15^{\circ} = 0.9371$ ; opt. rot.  $+9^{\circ}40'$ . Soluble in 2 to 2.5 volumes and more of 70 per cent alcohol; after adding about 6 volumes opalescence occurs. The oil contains 5.57 per cent menthol as ester, and 12.9 per cent total menthol. To all appearances we have here a kind of pennyroyal oil, to which the odour also points.

We further received the following oils from Messrs. Gómez Acebo & Co. of Madrid:

1. **Oil of Sweet Marjoram.** Spec. grav. at  $15^{\circ} = 0.9152$ ; opt. rot.  $+0^{\circ}39'$ . Soluble in 2.5 volumes and more of 70 per cent alcohol. Saponification number = 18.39.

2. **Oil of Spike.** Specific gravity at  $15^{\circ} = 0.905$ ; optical rotation  $-1^{\circ}47'$ . Soluble in 10 to 12 volumes of 60 per cent and 1.5 to 2 volumes of 70 per cent alcohol. Acid number 0.8; saponification number 9.28. Upon distillation of the oil, the first 10 per cent of the distillate show an optical rotation of  $+1^{\circ}$ .

3. **Oil of Sage.** Specific gravity at  $15^{\circ} = 0.9107$ ; opt. rot.  $+2^{\circ}56'$ . Soluble in one volume and more of 80 per cent alcohol. Saponification number 5.78.

4. **Oil of Rosemary.** Specific gravity at  $15^{\circ} = 0.9074$ ; opt. rot.  $+13^{\circ}36'$ . Soluble in 1 to 1.5 volume and more of 80 per cent alcohol. Saponification number 3.36. Upon distillation of the oil, the first 10 per cent of the distillate show an optical rotation of  $+4^{\circ}32'$ .

5. **Oil of Stoechas.** Specific gravity at  $15^{\circ} = 0.9266$  opt. rot.  $+7^{\circ}50'$ . Soluble in 0.7 volume and more of 80 per cent alcohol. Acid number 2.56, saponification number 20.48. It is probably a question of the oil of *Lavandula Stoechas*, or *L. dentata*<sup>1)</sup>.

All the five oils are rich in cineol, and they differ but slightly in the odour, which in every case has the character of rosemary oil.

As a further novelty we received from the South of France an oil designated as "petit-grain mandarinier", which undoubtedly is obtained from the twigs, leaves and unripe fruits of the mandarin tree. The properties were as follows: Specific gravity at  $15^{\circ} = 1.005$ ; optical rotation  $+7^{\circ}19'$ ; soluble in about 9 volumes 80 per cent alcohol. The oil is faintly acid, and has a high ester-content (saponification number 159.1). It has a strong bluish fluorescence and a neroli-like odour, which, owing to an accompanying odour like cresol, appears less pleasant. Phenol-like bodies could be isolated from the oil, but in the small sample the quantity of these was so minute, that a closer examination could not be made.

From the same source a sample of oil of "petit-grain citronnier" has been obtained, which differs in a somewhat marked degree from a sample received several years ago<sup>2)</sup>. It had the following properties: Specific gravity at  $15^{\circ} = 0.8869$ ; optical rotation  $+20^{\circ}21'$ ; soluble in 0.2 volume and more of 90 per cent alcohol. Acid number 3.3; saponification number 45.7. In this oil, like in that received in 1896, citral could be detected.

The last annual report of the Botanical Gardens at Buitenzorg, from which we have already quoted so many important communications on phytochemical and phytonomical subjects, contains information which is almost exclusively of interest for botanists.

A matter worth mentioning is, that at Buitenzorg it has also been observed, that Java citronella oil, such a favourite on account of its high content of citronellal and geraniol, is not always of the same

<sup>1)</sup> Report, October 1889, p. 54.

<sup>2)</sup> Report, October 1896, p. 62.

composition. For example, plants which at first yielded an oil with a total content of citronellal and geraniol of 90 per cent, contained only a total of 65.85 per cent of these two compounds when cut in November. In order to discover the cause of the diminution of these valuable constituents, the oil obtained in distilling leaves 1 $\frac{1}{2}$  months old was collected in four fractions. It was then found that the first fraction had the highest geraniol-content.

Further examinations will be made to ascertain in how far the time of the year, the age of the material used, and the method of distillation itself affect the geraniol-content.

**Knotgrass Oil.** During the examination of the constituents of the herb of *Polygonum Persicaria* L., which is much used in Russia as a popular remedy, P. Horst<sup>1)</sup> discovered a very small quantity (0.053 per cent) of essential oil. The bulk consisted of a mixture of volatile fatty acids, of which acetic acid and butyric acid were isolated in the form of their silver salts.

The remaining portion of the essential oil contained a crystalline camphor-like substance, persicariol, and a liquid body. The material at disposal was not sufficient for a complete study, and the author proposes to make a further examination later on.

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## Notes on recent scientific work concerning terpenes and terpene derivatives.

In a treatise dealing with the determination of specific gravities<sup>2)</sup>, O. Schreiner recently declared himself in favour of determining this constant at a temperature higher than 15°. As it is not, however, always possible to adhere to the temperature of 15° which is required in the majority of cases, the author, in order to render comparisons with other determinations possible, undertook jointly with W. R. Downer the work of determining the specific gravities (compared with water of the same temperature) of a number of essential oils, in Ostwald's pycnometer, at 15°, 20° and 25°<sup>3)</sup>, and of calculating therefrom the variations which these oils undergo for every degree within the given interval of 10°. From these determinations it appears that the variations in the specific gravities of essential oils for every degree are comparatively small, and remain almost the same for each oil between

<sup>1)</sup> Chemiker-Zeitung **25** (1901), 1055.

<sup>2)</sup> Pharm. Review **18** (1900), 457.

<sup>3)</sup> Pharm. Archives **4** (1901), 165.

15° and 25°. The differences which the individual oils show when compared one with the other are also unimportant; only cade and wintergreen oils show fairly large variations. The mean of all the values is found to be, for the temperatures between 15° and 25°, a decrease of 0.00064 for every degree increase in the temperature.

In connection herewith Schreiner and Downer further communicate the coefficients of expansion of those oils of which they have determined the specific gravities.

Although this process may provide a means of calculating the specific gravity for another temperature than the one at which it had been determined, it should not be lost sight of that it can only be approximately accurate; for exact determinations it would be indispensable to take the specific gravity at the required temperature.

In recent times methods for examining essential oils have frequently been recommended, in which sufficient regard has not been paid to the character of these bodies as mixtures which differ slightly in their compositions. For example, Dowzard<sup>1)</sup> recommended the determination of viscosity, especially of lemon oil, and Jeancard and Satie<sup>2)</sup> ascertained the surface tension and viscosity of different essential oils, in order to be able to use them as standards in judging. If we do not always take a definite stand in such matters — although we have tested Dowzard's method, and found it hardly reliable — it is because we consider that such methods are condemned by themselves in course of use, and for that reason disappear as suddenly as they have made their appearance.

A few years ago M. Duyk<sup>3)</sup> recommended in a treatise a concentrated solution of sodium salicylate for the separation of certain oxygenated compounds of essential oils from the terpenes, etc., which are present at the same time. This solvent has now been employed by Charabot and Hébert<sup>4)</sup> in their examinations concerning the process of esterification within the plant, in order to separate the non-esterified alcohol from the esters, greatly to the detriment of the correctness of their results; for Darzens and Armingeat's<sup>5)</sup> treatise on this subject would have shown clearly that the results obtained with this solvent cannot even lay claim to being called "approximately correct". Similar observations have also been made by ourselves, and others who have used this method once may have had the same experience as we.

<sup>1)</sup> Report April 1901, 31.

<sup>2)</sup> Bull. soc. chim. III. 25 (1901), 519.

<sup>3)</sup> Bull. de l'acad. roy. de méd. de Belgique 1899.

<sup>4)</sup> Bull. scient. et industriel de Roure-Bertrand, Oct. 1901, 4 and 13.

<sup>5)</sup> Bull. soc. chim. III. 25 (1901), 1053.

With regard to the determination of the index of refraction we also adhere to the position which Gildemeister and Hoffmann, in their work on volatile oils, have described in detail. We still believe that the refractive power is not so well suited for detecting adulteration as the traditional standards for estimating the value, such as specific gravity, rotatory power, etc. In the course of the last few years several works referring to this question have appeared, in which the determination of this constant is recommended, for example Hartwich's<sup>1)</sup> work, and especially that by Utz<sup>2)</sup>, and this has induced us to go more fully into this matter. But although in Utz's latest work the author in conclusion expresses the hope that the determination of the index of refraction may become as indispensable as the ascertaining of the specific gravity and optical rotation, that work yet shows that the conclusions at first arrived at by the author on the strength of his determinations, have not altogether proved correct.

We are still engaged in collecting material, and after completion of our experiments will return to the subject.

Saltlike compounds of oxygenated substances free from nitrogen have already been known for some time. Whilst at one time they were considered to be either molecular compounds, or chemical compounds in the earlier sense, the attempt has recently been made to explain their nature by the quadrivalent character of oxygen, it being thought that the behaviour of the oxygen atom towards acids could as well be quadrivalent, as nitrogen in ammonia quivalent. During an investigation made in another direction, v. Baeyer and Villiger<sup>3)</sup> had occasion to pay special attention to the quadrivalent character of oxygen; they then found that the simple atom of oxygen is capable of forming salts (i. e. addition of acids), in every form in which it occurs in organic chemistry, and that it is not only in exceptionally favourable cases possible to obtain well-characterised compounds, but, with few exceptions, in every instance, if only the appropriate acid is selected and the work is carried on under suitable conditions.

One of the best-known examples of this kind is cineol, of which the phosphoric acid compound and also, as has recently become known, the arsenic acid addition product, are used for the production of this body in the pure state. Phosphoric acid compounds of aromatic ketones, aldehydes and esters have also been described not very long ago by Klages and Raikow.

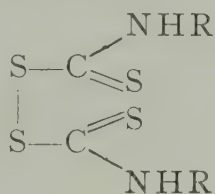
<sup>1)</sup> Apotheker-Ztg. **14** (1899), 584.

<sup>2)</sup> Apotheker-Ztg. **15** (1900) 441 and 453; **16** (1901), 742.

<sup>3)</sup> Berliner Berichte **34** (1901), 2679. — It would be better not to designate the unsaturated condition of oxygen as "basic". Compare also Vorländer, Liebig's Annalen **320** (1902), 116.

v. Baeyer and Villiger, however, did not select phosphoric acid for their addition-experiments, but chiefly hydroferro- and -ferricyanic acids, as also hydrocobalticyanic acid. We only mention such of the very numerous observations communicated, as refer to compounds of the terpene series. For example, cineol combines with all three above-named acids; of the secondary alcohols borneol reacts specially, menthol and tetrahydrocarveol less so. Of the monocyclic saturated ketones, 1,3-methyl cyclohexanone, menthone and tetrahydrocarvone were tested with positive results. Ketones capable of addition are camphor, fenchone and carone of the dicyclic saturated kind, carvenone i-dihydrocarvone and carvone of the unsaturated mono-cyclic kind.

J. v. Braun and K. Rumpf<sup>1)</sup> have, by condensation of amines of the terpene series with carbon disulphide, produced salts of dithiocarbamic acid, from which are formed by oxidising agents (I or H<sub>2</sub>O<sub>2</sub>) thiuram disulphides of the general formula:



These disulphides, dissolved in alcoholic potassa, yield with iodine the corresponding mustard oils S : C : N · R, which unite with the original bases to dialkylated sulpho-ureas; the latter could also be obtained directly by slightly heating the thiuram disulphides. With aniline the mustard oils combined to phenylated sulpho-ureas, which were identical with those obtained from phenyl mustard oil and terpene bases. These sulpho-ureas, like the aliphatic and the aromatic representatives of this class of bodies, react readily with halogen alkyls.

These reactions were studied on the following bases: methyl cyclohexylamine, pinylamine, camphylamine, thujylamine, and l-menthylamine.

## Hydrocarbons.

The conversion of some terpenes and camphors in the animal organism is the subject of several works by H. Hildebrandt<sup>2)</sup>, E. Fromm and H. Hildebrandt<sup>3)</sup>, and E. Fromm and P. Clemens<sup>4)</sup>.

<sup>1)</sup> Berl. Berichte **35** (1902), 130.

<sup>2)</sup> Arch. f. exper. Pathologie u. Pharmakologie **45** (1900), 110.

<sup>3)</sup> Hoppe-Seyler's Ztschr. f. physiolog. Chemie **33** (1901), 579.

<sup>4)</sup> Ibidem **34** (1902), 1.

The authors have elaborated previous works by other investigators of this domain, and have traced the fate of the following terpenes and terpene derivatives in the organism of dogs and rabbits: geraniol, citral, linalol, citronellol, citronellal; cymene<sup>1)</sup>; pinene, phellandrene, camphene, sabinene, sabinol, thujone<sup>2)</sup>, menthol and borneol<sup>3)</sup>.

On account of a certain analogy in the behaviour of ring-shaped compounds, general propositions could be laid down for the changes which occur in the animal body: in the urine, combined glycuronic acids occur after administration of cyclic terpenes and camphors, of which one term is a terpene derivative ("terpenol") containing the hydroxyl group. The true terpenes  $C_{10}H_{16}$  in this case absorb one atom of oxygen and are converted into terpenols  $C_{10}H_{15}OH$ , which leave the animal body combined with glycuronic acid  $C_6H_{10}O_7$ . The compounds of the formula  $C_{10}H_{16}O$  behave in a different manner: sabinol, which already contains a free hydroxyl group, is not hydroxylised further, but combines as such with glycuronic acid. From camphor and fenchone earlier investigators had obtained "campherol" and "fenchonol". Thujone adds the elements of water, and is consequently converted by hydration into a compound containing hydroxyl. Borneol and menthol, as alcohols, remain unchanged, like sabinol.

The "terpenol"-glycuronic acids could only be isolated in a few cases either free or in the form of salts. Thus borneol- and menthol-glycuronic acids, and further a few salts of these acids and the potassium salt of the acid from thujone hydrate, were isolated and analysed. Boiling with dilute mineral acids decomposes all these acids into their components; the "terpenol" is thereby generally converted with loss of water into the hydrocarbon  $C_{10}H_{14}$ , in which the authors recognised cymene. In a few cases acids and phenols are also formed in the process of decomposition. From camphene was obtained "camphenol", an oil of the boiling point  $202^{\circ}$  to  $204^{\circ}$ . Menthol and borneol were recovered unchanged.

Cymene was oxidised in the animal body into cumic acid, a conversion which is recommended for the detection of sabinol poisoning, by administration of the cymene obtained from the urine, and examination of the secondary digestion-product.

Of the compounds with open carbon chain, only conversion-products of geraniol and citral were obtained, — in both cases a dibasic double unsaturated acid of the formula  $C_{10}H_{14}O_4$ , with a melting point  $187^{\circ}$ . But only "citral a"<sup>4)</sup> yielded this acid; when "citral b" was administered,

<sup>1)</sup> Arch. f. exper. Pathologie u. Pharmakologie **45** (1900), 110.

<sup>2)</sup> Hoppe-Seyler's Ztschr. f. physiolog. Chemie **33** (1901), 579.

<sup>3)</sup> Ibidem **34** (1902), 1.

<sup>4)</sup> Tiemann, Semmler and Kerschbaum, Berl. Berichte **31** (1898), 2313; **32** (1899), 827; **33** (1900), 877.

the occurrence of the acid was not observed, and the same happened when linalol, citronellol and citronellal were given.

**Pinene.** By boiling pinene with crystallised arsenic acid, Genvresse<sup>1)</sup> obtained an oil with an essentially higher boiling point, higher specific gravity, and larger refraction, from which he isolated, by fractionating, 60 per cent of an oil of the boiling point  $177^{\circ}$  to  $180^{\circ}$ , at 740 mm pressure. This fraction consisted of laevogyre terpinene (rotation =  $10^{\circ} 47'$  and  $10^{\circ} 21'$  in a tube of 200 mm) which was identified by the nitrosite melting at  $155^{\circ}$ . He further detected cymene in the lower-boiling portions, and terpineol in the fractions boiling above  $180^{\circ}$ . Genvresse and Langlois obtained in the same manner terpinene from limonene. The author recommends this method for the production of terpinene on a large scale.

In continuation of their examinations on the subject of sesquiterpenes, O. Schreiner and Edw. Kremers have again published a work which deals in some detail with the characterisation and classification of sesquiterpenes<sup>2)</sup>. After a retrospect on the history and systematisation of the terpenes, the authors discuss exhaustively the conditions which come under consideration for the sesquiterpenes.

As hydrocarbons  $C_{15}H_{24}$  of the general saturation formula  $C_nH_{2n-6}$  they should be arranged in the following five groups:

1. Compounds with an open chain of carbon atoms and four double linkings; 2. monocyclic compounds with three double linkings; 3. dicyclic compounds with two ethylene linkings; 4. tricyclic compounds with a single, and finally 5. tetracyclic compounds without any such linking.

Group 2 can be sub-divided according as 3, 4, 5 or 6 carbon atoms are forming the ring. Similarly the groups 3, 4 and 5 can be sub-divided according to the number of carbon atoms combined in the ring. A further division can also be made in accordance with the number of double linkings in the ring.

Representatives of the fifth group are as yet unknown, but possibly some heavy sesquiterpenes may belong to it which yield no addition products with nitrosyl chloride. To the tricyclic compounds may perhaps be numbered clovene; to the dicyclic group belongs undoubtedly cadinene, also caryophyllene, and probably humulene.

<sup>1)</sup> Compt. rend. **134** (1902), 360.

<sup>2)</sup> Pharm. Archives **4** (1901), 141 and 161.

Representatives of the monocyclic compounds are probably zingiberene and Semmler's *Carlina*-sesquiterpene, if the latter is not as a matter of fact identical with zingiberene. A chain-like arrangement of carbon atoms may perhaps be assumed in the light sesquiterpene isolated from citronella oil (Report October 1899, page 23).

In connection with these theoretic considerations, the authors report on zingiberene, the sesquiterpene of ginger oil already described by H. v. Soden and W. Rojahn. Obtained from the oil by fractional distillation in vacuo, it boils at 32 mm pressure at 160—161°, and has a specific gravity of 0.8731 at 20°;  $[\alpha]_D = -73.38^\circ$ , and  $n_D = 1.49389$ ; it therefore shows approximately the same constants as those indicated at the time by v. Soden and Rojahn. Next follow details about derivatives of zingiberene, for example the crystallised dihydrochloride (melting point 168 to 169°), the nitrosite (melting point 97—98°), the nitrosate (melting point 86—88°), and the nitrosochloride (melting point 96—97°). Kremers and Schreiner correct at the same time one of their earlier notes on a hydrochloride of caryophyllene by stating that this compound is a dihydrochloride; when heated with glacial acetic acid and sodium acetate, a sesquiterpene can be regenerated from it, which, according to its constants, is neither identical with caryophyllene, nor with clovene.

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Cadinene. Cathelineau and Hausser describe in their work "Études sur l'huile de cade"<sup>1)</sup> a method for producing cadinene hydrochloride. The portions of cade oil which are not dissolved in soda liquor, are distilled with steam after adding a 40 per cent solution of soda. The oil thus obtained is made into an emulsion with 3 parts of 90 per cent alcohol, and while the mixture is cooled a strong current of dry hydrochloric acid gas is passed through it up to saturation. After standing for 24 hours the alcohol is decanted from the lower layer, which represents a pasty mass of cadinene hydrochloride; the crystalline mass is allowed to drain on cotton wool, and then washed with alcohol containing hydrochloric acid. By once more working up the drained oil a further small quantity of the hydrochloride is obtained. The residue is treated with dry ammonia at 245 to 250°, in order to decompose the products containing hydrochloric acid. The product of reaction is washed with water, and repeatedly distilled. The fraction having a boiling point of 268—275° still contains cadinene, which may be obtained by the above method or in the usual manner (by dissolving in ether and introducing hydrochloric acid gas).

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<sup>1)</sup> Bull. soc. chim. III. 25 (1901), 931.

This complicated method does not appear to have any advantages over the one employed hitherto.

An oil which was found to be a particularly suitable crude material for the production of cadinene, was one distilled by us from the wood of a species of *Cedrela* from Nicaragua. Its constants are:  $d_{15}^{\circ} = 0.9212$ ;  $\alpha_D = -46^{\circ}50'$ . The bulk of the oil consists of cadinene; about 70 per cent of it pass over, at 5 mm, between  $130$  and  $135^{\circ}$ ; this is followed by a thick viscid liquid which appears to be cadinene already partly resinified. A resinous residue remains in the flask. If the oil, diluted with 2 parts ether, is saturated with hydrochloric acid gas, it will be found that already after standing quietly for a few hours, abundant quantities of the hydrochloride separate out in a fairly pure state. About the same quantity is obtained after evaporating the ether from the mother liquor. The hydrochloride melts at  $116.5-117^{\circ}$ , and is laevogyre. For the purpose of comparing the optical activities, the following hydrochlorides were prepared:

Hydrochloride from:	Oil of Cedarwood from Cuba <sup>1)</sup>	Oil of Cedrela wood from Nicaragua	Peppermint Oil	Camphor Oil
Meltingpoint	$117-118^{\circ}$	$116.5-117^{\circ}$	$117-118^{\circ}$	$117-117.5^{\circ}$
$\alpha_D$ in a 5 per cent solution of ether	$-1^{\circ}34'$	$-1^{\circ}36'$	$-1^{\circ}50'$	$-1^{\circ}30'$

The cadinene regenerated from the hydrochloride of cedrela wood oil had the following constants:

Boiling point at 4 mm =  $128-130^{\circ}$ ;  
 $d_{15}^{\circ} = 0.9244$ ;  $\alpha_D = -99^{\circ}6'$ .

We have, unfortunately, only a small quantity of this oil at our disposal.

F. W. Semmler<sup>2)</sup> reports on experiments in the terpene series, especially on the attachment of hydrogen to myrcene. In terpenes with only one ethylene linking the reduction with sodium and alcohol does not succeed, — in terpene compounds which contain besides a ketonic oxygen atom it succeeds only then, when the double linking

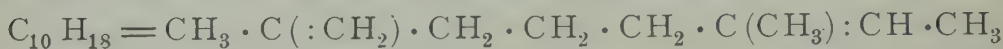
<sup>1)</sup> Compare Report April 1892, p. 41.

<sup>2)</sup> Berl. Berichte 34 (1901), 3122.

is close to the CO, that is to say, when, according to Thiele's theory, one has to deal with a system of adjoining, conjugated linkings. As the cyclic terpenes, such as limonene, terpinene, terpinolene, carvestrene and pseudocarvestrene cannot be reduced by sodium and alcohol, Semmler concludes that in those compounds the double linkings are not adjoining.

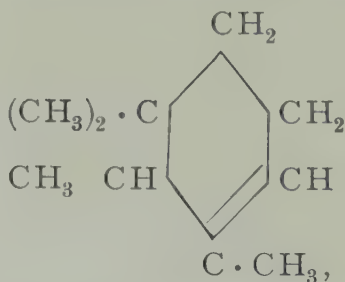
Olefinic myrcene, however, is capable of being reduced by sodium and alcohol; for this reason it must contain two adjoining double linkings in the sense of Thiele's theory, and may therefore correspond to the formula  $\text{CH}_3 \cdot \text{C}(:\text{CH}_2) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(:\text{CH}_2) \cdot \text{CH}:\text{CH}_2$ .

This hydrocarbon, boiling at atmospheric pressure at  $170-172^\circ$  without any decided decomposition, when treated with sodium and alcohol absorbs hydrogen, and yields a dihydromyrcene



which, according to Thiele's theory, occupies the non-reduced double linking in intermediate position to the two previously present adjoining linkings. This hydrocarbon absorbs only 4 atoms of bromine, and yields then an oily tetrabromodihydromyrcene  $\text{C}_{10}\text{H}_{18}\text{Br}_4$ .

Dihydromyrcene, the properties of which are very similar to those of linalolene, can be converted (most readily by glacial acetic acid and sulphuric acid) into a cyclic hydrocarbon, cyclodihydromyrcene:



which, owing to the fact that it contains now only one double linking, absorbs only one molecule of bromine. When cyclodihydromyrcene is oxidised, it yields a ketonic acid  $\text{C}_{10}\text{H}_{18}\text{O}_3$  which has not yet been examined more closely; dihydromyrcene, on the other hand, when treated with permanganate solution, yields no longer (like myrcene) succinic acid, but laevulic acid, and, moreover, a ( $\delta$ -[?]) diketone  $\text{C}_7\text{H}_{12}\text{O}_2$ , and also always acetone, from which Semmler concludes that crude myrcene also contains the hydrocarbon



The reduction method therefore seems to offer a further means of solving certain constitution questions, as it apparently indicates, if several double linkings are present, where they are adjoining, and where not.

## Alcohols.

Linalol. As mentioned by us in our Report of October 1901 p. 71, the formula proposed by Tiemann for linalol has been claimed by Barbier for myrcenol, the alcohol formed by hydration from myrcene. The last-named investigator thereby found himself obliged to publish a fresh formula for linalol; this he has recently done in a communication on the constitution of linalol (licareol)<sup>1)</sup>.

According to Barbier, the linalol usually prepared from linaloe oil or the oil of *Licari kanali*, is a mixture of natural linalol and l-terpineol (!) besides a small quantity of active myrcenol and another unsaturated body  $C_{10}H_{18}O$ . By treating this mixture with phthalic or succinic anhydrides, it yields a linalol which is pure, but yet not a uniform body, as is shown by the variability of the rotatory power. Pure natural linalol is as yet unknown, and we are therefore not yet able to express an opinion on its optical activity; on the contrary, the observation made by Stephan, that geranyl alkali phthalate, when treated with water vapour, yields inactive linalol, would seem to indicate that this alcohol is, as a matter of fact, optically inactive. Barbier has also been unsuccessful in decomposing linalyl succinate of sodium by cultures of *Penicillium glaucum*, which he should have been able to do if the inactive linalol were a racemic compound.

According to Barbier, in order to ascertain the constitution of linalol, more attention should be paid to the products formed in the oxidation and other reactions. But these are mostly the same compounds which geraniol also yields; for this reason, the carbon atoms in the two alcohols must be arranged in the same manner, that is to say, the constitutional formula of geraniol  $(CH_3)_2 \cdot C : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH \cdot CH_2 OH$  must also apply to linalol, and both alcohols therefore be considered as stereo-isomerides.

It is at the least questionable whether one is justified in considering linalol, as Barbier does, as optically inactive; it is scarcely right to attribute the rather considerable rotation which this alcohol shows, both in the lævogyre and in the dextrogyre modification, to isomerides present in it. If linalol were actually a mixture of "natural" linalol and l-terpineol (what Stephan, however, has never stated) and moreover contained myrcenol, the natural linalol should have a much lower specific gravity and a lower boiling point than has hitherto been accepted. Besides, the oxidation, which yields citral and the products of decomposition of the latter, has mostly been performed with chromic acid mixture, when, as experience shows, constitutional changes are not excluded. It would, therefore, require further proofs, before Tiemann's formula for linalol is abandoned.

<sup>1)</sup> Bull. soc. chim. III. 25 1901, 828.

On the other hand, we would propound the question whether the myrcenol produced by Barbier, to which the formula of linalol would belong, is not rather a mixture of linalol and terpineol. This would, for example, explain the high specific gravity of myrcenol. Semmler, in his investigations on myrcene, has also come to the conclusion that in hydrating this hydrocarbon a uniform product is not formed. We propose in due time to return to this subject.

## Aldehydes.

**Citronellal.** In endeavouring to ascertain the constitution of citronellal from the products of decomposition obtained in the oxidation of this body, Harries and Schauwecker have come to the conclusion,<sup>1)</sup> that the principal constituent of commercial citronellal is an aldehyde of the formula



If citronellal dimethyl acetal is treated with an aqueous solution of permanganate, it yields acetone and the dimethyl acetal of the semi-aldehyde of  $\beta$ -methyl adipic acid



A glycol of this acetal, which is formed in such an oxidation process up to 30—40 per cent, but in still larger proportion on oxidation in acetone, should, if it originates from an acetal



have the formula



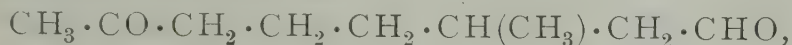
and should, on further oxidation, split up into the semi-aldehyde of  $\beta$ -methyl adipic acid (or its acetal), and acetone. Such a conversion could, however, not be observed. With permanganate, the glycol is exceedingly stable, but when treated with chromic acid and glacial acetic acid, it yields a number of new products, the origin of which may be expressed by the following formula:



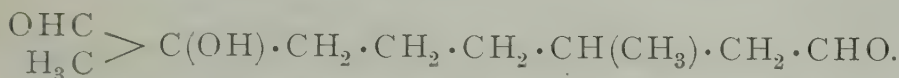
There are chiefly two compounds which could be separated by fractional distillation in vacuo; the one boils at about 115 to 118° at 16—17 mm pressure, reduces Fehling's solution on being heated, and has the empirical composition  $\text{C}_9\text{H}_{16}\text{O}_2$ ; the other boils at 10 mm pressure at 130 to 140°, reduces Fehling's solution already at ordinary temperature, and has the composition  $\text{C}_{10}\text{H}_{18}\text{O}_3$ , and may

<sup>1)</sup> Berl. Berichte **34** (1901), 2981.

therefore be looked upon as the first oxidation product of the glycol. Both compounds are free aldehydes without acetal groups; they correspond probably to the formulæ:



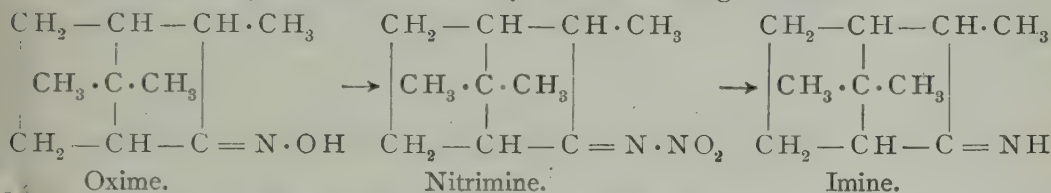
and



Their formation may readily be explained by the last-mentioned formula of dioxydihydrocitronellal acetal.

### Ketones.

Fenchone. If nitrous acid acts on fenchone oxime, there results, besides fenchimine nitrate, fenchone nitrimine, which on treatment with concentrated ammonia liquor is converted into fenchimine  $\text{C}_{10}\text{H}_{16}\text{NH}$ . The process may be illustrated by the following formulæ:



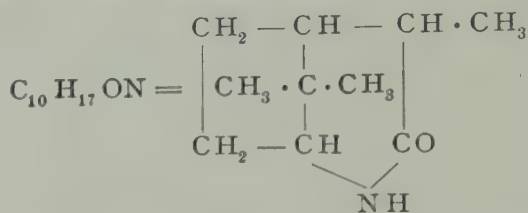
According to Mahla<sup>1)</sup> fenchimine boils at 16 mm pressure at  $83^\circ$ . Its specific gravity is 0.9322 ( $11.5^\circ$ ), the rotation  $+76.30^\circ$  ( $19.5^\circ$ ), refraction  $40^\circ 43'$  ( $17^\circ$ );  $n_D 17^\circ = 1.47809$ , molecular refraction = 45.857. The hydrochlorid melts at  $278^\circ$ . With methyl iodide in dry ether solution, fenchimine forms crystalline methyl fenchimine iodide. The conversion of fenchimine into dihydrofencholene nitrile,  $\text{C}_{10}\text{H}_{17}\text{N}$ , with disruption of one ring, proceeds in an entirely analogous manner to that of camphorimine into dihydrocampholene nitrile;<sup>2)</sup> there is also formed, under the influence of the oxygen of the air, an oxydihydrofencholene nitrile  $\text{C}_{10}\text{H}_{17}\text{ON}$ . The first-named product boils, at 23 mm pressure, at  $98-104^\circ$ ; the specific gravity is 0.8951 ( $16.5^\circ$ ), the rotation  $+25^\circ$  ( $19^\circ$ ), the refraction  $45^\circ 46'$  ( $17.5^\circ$ );  $n_D = 1.44743$ . The nitrile readily volatilises with water vapour; concentrated potash liquor converts it into the amide  $\text{C}_{10}\text{H}_{19}\text{NO}_2$ , of the melting point  $130.5^\circ$ , which is saponified by concentrated hydrochloric acid into dihydrofencholenic acid, boiling at  $145-146^\circ$ , at 13 mm pressure. Mahla prepared the silver and ammonium salts of this acid; its specific gravity is 0.9816 ( $15^\circ$ ), the rotation  $\alpha_D = +4.30^\circ$  ( $15.5^\circ$ ).

Oxydihydrofencholene nitrile is an oil boiling at  $153-154^\circ$ , at 23 mm pressure, of the specific gravity 0.9792 ( $15^\circ$ ). Rotation

<sup>1)</sup> Berliner Berichte **34** (1901), 3777.

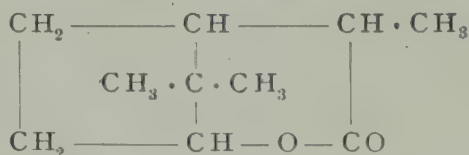
<sup>2)</sup> Berliner Berichte **33** (1900), 1929.

$\alpha_D = -8^\circ$  ( $18^\circ$ ); refraction =  $43^\circ 6'$  ( $18^\circ$ );  $n_D 18^\circ = 1.46464$ . When treated with 30 per cent potash liquor the amide is formed of the melting point  $78^\circ$ , and from this, with dilute hydrochloric acid, by the application of heat, oxydihydrofencholenic acid lactame:



of the melting point  $136-137^\circ$ . This body is identical with Wallach's  $\beta$ -fenchone isoxime<sup>1)</sup>.

As a second product of the action of potash liquor on oxydihydrofencholene nitrile, Mahla obtained an acid  $\text{C}_{10}\text{H}_{18}\text{O}_3$  of the melting point  $113-114^\circ$ . As it had the property of very readily forming a lactone of the formula  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , it may be concluded that it represents  $\delta$ -oxydihydrofencholenic acid. The solution of its ammonium salt yields with silver nitrate a colourless silver salt, and with acetate of copper a bluish green copper salt. Its lactone melts at  $72^\circ$ , and boils at 10 mm pressure above  $130^\circ$ ; the constitution of the latter is as follows:



Methyl heptenone. Wallach's 52<sup>nd</sup> treatise<sup>2)</sup> on the knowledge of terpenes and essential oils contains some interesting observations. This investigator had already shown on a previous occasion that from methyl heptenone oxime, by means of phosphorus pentoxide, a base of the composition  $\text{C}_8\text{H}_{13}\text{N}$ , probably a dihydrocollidine, can be obtained. This base can be converted by reduction into a trimethyl piperidine  $\text{C}_8\text{H}_{17}\text{N}$ , which has the same composition as coniine, and whose isomerism with this alkaloid is based on the fact that it is a trimethyl instead of a propyl piperidine. This base  $\text{C}_8\text{H}_{16}\text{NH}$  shows also exactly the same behaviour as that which might be expected from a piperidine base; it can, namely, be converted in a corresponding manner into a hydrocarbon  $\text{C}_8\text{H}_{14}$  isomer with conylene.

The second part of the treatise contains information on a brominated methyl heptenone  $\text{C}_8\text{H}_{13}\text{OBr}$  and its products of conversion (oxime, semicarbazone, and the compounds formed therefrom). But

<sup>1)</sup> Liebig's Annalen **269** (1892), 332.

<sup>2)</sup> Liebig's Annalen **319** (1901), 77.

the third and last part is of particular interest; in this the author deals with the conversion of methyl heptenone into a new isomeride. The methyl heptenylamine  $C_8H_{17}N$  formed by reduction of the methyl heptenone oxime, can be converted into a base  $C_8H_{15}N$  containing less hydrogen, by adding bromine to the monohydrochloride of the original base  $C_8H_{17}N$ , and evaporating to dryness the aqueous solution of the addition product. There is then formed, whilst hydrohalogen is split off, the salt of a new base  $C_8H_{15}N$ , which behaves in many respects in a different manner from all hitherto known bases, and which therefore in a certain degree represents a new type. If it is submitted to the action of nitrous acid, it yields a ketone  $C_8H_{14}O$  whose boiling point is constant at  $161$  to  $162^\circ$ , and whose odour, while reminding of that of natural methyl heptenone, can yet be clearly distinguished from it. On oxidation the new methyl heptenone yields oxalic and isobutyric acids; for this reason it appears to differ from natural methyl heptenone, not by the position of the ethylene linking, but rather by that of the oxygen atom.

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**Aubépine (Anisic aldehyde).** Since the manufacture of this article has been taken up by the wholesale chemical manufacturers, and a large number of makers participate in the unimportant sale, the value, like that of other similar products, has been on the down grade. Champion is he who produces the best quality. The intelligent perfumer will not fail to make comparisons before he makes his choice.

**Citral.** The high value of lemongrass oil is not yet represented correctly by the price of this product. Before the present tide of the market set in, we had made large purchases, and were thereby in a position to make favourable offers.

Our new installation enables us to increase the production of citral as desired. In view of the low quotations of lemon oil, however, the conditions for the sale are at present not particularly favourable.

**Coumarin.** The prices of this preparation have undergone a further decline in the course of the last six months, and have now probably reached the lowest limit. It may be mentioned that this slump has not appreciably affected the quotations of other drugs containing coumarin, as for example tonka beans; on the contrary, the one exists alongside the other, and the fear that the latter would be entirely supplanted by coumarin, has not been confirmed.

Under the present conditions the equivalent of 1 kilo tonka beans, value about 7/—, in coumarin is about 6 d.

It is probably generally known, that our indigenous coumarin plants, such as *Asperula* and *Anthoxanthum*, only commence to give forth the odour of coumarin when they are withering, and that the odour is most intense when the plant is in the dried state. A similar behaviour was observed by H. Molisch<sup>1)</sup> with one of the acanthaceæ, *Peristrophe angustifolia*, a native of Java, which in our country is also frequently cultivated. Dried specimens of this plant gave off a strong odour of coumarin, which could not be noticed in living specimens. From the fact that the coumarin, which could be identified as such with certainty, only occurs after the plant has died, Molisch concludes that a glucoside-like body is present, which is decomposed by a simultaneously present ferment, in the same manner as amygdalin is split up by emulsin. If, namely, the leaves of the living plant are immersed in boiling water or in 95 per cent alcohol, that is to say are submitted to conditions under which ferments are usually destroyed, they remain odourless even after being dried.

Similar observations had already been made earlier by Behrens with *Ageratum mexicanum* which also contains coumarin; they also remind strongly of the processes which occur in the fruit of vanilla.

**Eucalyptol, pure cryst. (Cineol).** The manufacture of this body is now carried on by us on a large scale, and any desired quantity can be supplied promptly. It is hoped that the considerable reduction in the price may lead to a gradual cessation of the use of eucalyptus oil, and to the substitution in practice of the pure eucalyptol. If the latter were included in the various pharmacopœias, it would be an opportune addition. The 1890 edition of the Pharmacopœia of the United States has led the way in this as in many other respects.

Our product has a melting point of  $-1^{\circ}\text{C.}$ , and is optically inactive.

For ton contracts we could offer important advantages.

On account of its strongly disinfecting and pleasant refreshing action, pure eucalyptol should find a greater use than hitherto in the preparation of cosmetics, especially for disinfection of the mouth and teeth. It might also be employed with advantage in the form of lozenges, similar to peppermint lozenges, and the introduction of eucalyptol soap might be equally worth a trial.

As a matter of fact, the medicinal action of eucalyptol has not yet been sufficiently appreciated in Europe. It would probably be worth while to make a thorough study of this subject. For this purpose we shall be happy to supply samples.

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<sup>1)</sup> Ber. d. deutsch. botan. Ges. **19**, 530, according to the Apotheker-Zeitung **17** (1902), 46 and 138.

**Eugenol.** By means of distillation in vacuo we obtain our product in absolutely anhydrous form, and of a light colour. On the strength of prolonged observations we may add that, even when exposed to light, the colour does not darken.

K. Auwers and O. Müller<sup>1)</sup> have studied the behaviour of some bromides of eugenol and isoeugenol, and have found that only negative substituent in the  $\alpha$ -position (that is to say in this case bromine atoms) can give to a para-alkylated phenol the character of a pseudo-phenol. Dibromoeugenol dibromide, as a true phenol, is under certain conditions no doubt soluble in alkalis (contrary to the observations of other chemists), but in a short time decomposition occurs, with splitting off hydrobromic acid. Those compounds deriving from isoeugenol dibromide which still contain a bromine atom in the side chain, behave in a similar manner. Contrary to the phenol ethers examined by Hell<sup>2)</sup> and Wallach<sup>3)</sup>, of which the propenyl side chain is saturated with bromine, the dibromide of free monobromoisoeugenol with excess of sodium ethoxide is not converted into a ketone with the side chain  $\text{CO} \cdot \text{CH}_2 \cdot \text{CH}_3$ ; but there are formed, by substitution of both bromine atoms, dialkylated ethers of glycols, which also by gradual elimination first of the  $\alpha$ -, then of the  $\beta$ -bromine atom, can be produced with alcohol or sodium ethoxide. The  $\alpha$ -bromine atom is characterised by a powerful reaction-capacity, both in isoeugenol dibromide and monobromoisoeugenol dibromide; with cold alcohols, aqueous acetone, or with sodium acetate, bodies are formed which contain in the  $\alpha$ -carbon atom the corresponding residues. The bromine atom in the  $\beta$ -position on the other hand, only reacts on the application of heat with sodium methoxide or ethoxide, with formation of  $\beta$ -alkoxyl derivatives. Contrary to this behaviour of brominated isoeugenol compounds, is the stability of the  $\beta$ - $\gamma$ -bromine atoms of dibromoeugenol dibromide, which can be boiled without change with alcohols, aqueous acetone, or sodium acetate.

**Geraniol from Citronella Oil.** (German Patent No. 76435.) By means of improved technical appliances we now supply this beautiful body in exceptional quality, and are in a position to guarantee prompt delivery, even for large quantities.

**Heliotropin** (Piperonal). At the present wretched prices, the manufacture can now only pay if carried on on a large scale and

<sup>1)</sup> Berl. Berichte **35** (1902), 114.

<sup>2)</sup> Berl. Berichte **28** (1895), 2082; Hell and Portmann *ibid.* **29** (1896), 676.

<sup>3)</sup> Wallach and Pond, Berl. Berichte **28** (1895), 2714.

with every technical advantage. Such conditions are present in our new factory, and we defy any competition in this article. The quality of our product has reached the highest degree of perfection, and is universally appreciated. In face of this fact, the opinion, which still prevails in some rare cases, that the quality of the heliotropin formerly prepared from the piperine of pepper, is superior to our product, can no longer be maintained.

On account of its low price, heliotropin is now also used for perfuming technical products of low value; it is then frequently mixed with coumarin. It is further employed for perfuming high-quality note paper, post cards, dyes, such as laundry blue, etc., by which means these articles find a more ready sale. There is also an increasing tendency to perfume the cardboard boxes in which textile fabrics are packed. For this purpose heliotropin is dissolved in alcohol, and the solution is sprayed on the inner surface of the cardboard box, shortly before the goods are dispatched. In some cases it is already sufficient to perfume only the inside of the cover.

**Linalyl Acetate.** We would draw the attention of perfumers to this preparation, which we are now able to supply at a low price by means of a simplified manufacturing process.

Linalyl acetate, as is well-known, is the body which is justly considered to be the active principal constituent of bergamot oil. It is the factor by which the value of bergamot oil is judged, and is contained in that oil in the proportion of 30 to 40 per cent.

The product which we here recommend contains about 80 per cent linalyl acetate; the remainder of about 20 per cent consists of linalol, which is also present in the free state in bergamot oil, and which can only be removed by a troublesome process.

Linalyl acetate may consequently be said to represent concentrated bergamot oil, free from terpene, practically about  $2\frac{1}{2}$  times as strong as the ordinary good quality oil. At a selling price of 45/ — per kilo, bergamot oil in the form of linalyl acetate would come to about 18/ — per kilo. Although at the present time this price might not permit the use on a somewhat large scale, it is possible that under more favourable conditions the tables would be turned, and linalyl acetate would become available as a substitute for bergamot oil. For this reason alone the production of a cheap linalyl acetate should already be welcomed.

But in spite of the fact that from a financial point of view linalyl acetate is at a disadvantage as compared with bergamot oil, it could be used in perfumery in all cases where the bulk of the ordinary bergamot oil in the preparations is objectionable, for 250 grammes bergamot oil could be replaced by 100 grammes linalyl acetate.

It has another advantage in being absolutely colourless. It is also very probable that linalyl acetate could be used advantageously on a large scale by mixing it with another body, as for example with citrene, the terpene obtained in large quantities in the manufacture of terpeneless oil of lemon.

In the foregoing we only wish to make suggestions for determining by practical experiments whether linalyl acetate at the present quotations might not be used with advantage.

We shall be pleased to supply samples.

**Menthol.** Since our last Report the demand has continued very strong. Large quantities of the purified article have been sold, but, unfortunately, at unremunerative prices, as the difference in the quotations between the crude, moist article and recrystallised, dry menthol scarcely covers the expenses and loss of material.

We would here point out that many unpleasant experiences have resulted from working up crude menthol which has only been dried superficially; occasionally migraine pencils have acquired a yellow tinge, probably caused by small particles of oxide from the original tins.

The result of the previous year's distillation of peppermint oil in Japan was estimated at the end of October last at about 90000 cattiees or about 54000 kilos. How much of this quantity refers to menthol, and how much to oil, is impossible to ascertain. Nor can any information be obtained about the stocks in hand in Japan, as the number of exporters has increased considerably during the last few years, and a check on the figures has become much more difficult.

On the other hand, the shipments of crude menthol from Japan to the individual principal markets, were as follows for the 6 months ending 31<sup>st</sup> December 1901:

to Hong Kong . . . . .	15230 cattiees
„ New York . . . . .	14155 „
„ Hamburg . . . . .	4337 „
„ Havre . . . . .	2900 „
„ Bombay . . . . .	1374 „
„ London . . . . .	1988 „
„ Vancouver . . . . .	800 „
„ Portland . . . . .	450 „
„ Philadelphia . . . . .	360 „
„ Singapore . . . . .	139 „
„ Bangkok . . . . .	45 „

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Total 41778 cattiees,  
or 25066 kilos.

Total export of crude menthol in the year 1901:

from 1<sup>st</sup> January to 31<sup>st</sup> July . 11883 cattiees

„ 1<sup>st</sup> August to 31<sup>st</sup> December 41778 „

Grand total 53661 cattiees

or 32200 kilos.

These figures confirm in a striking manner what we said at the beginning. Such large quantities have not been shipped for a long time.

As to the probable movement of the prices in the near future, we consider a backward tendency out of the question so long as the brisk demand continues. We would much sooner expect a rise, as the great delays in recent shipments point to a lack of available material.

**Safrol.** The selling price of this body, discovered by us in camphor, has recently undergone no change. It is employed on a constantly growing scale for perfuming good quality soaps for domestic use, which it improves considerably by its strong odour.

The competing article from Japan has not yet appeared on the market. We calmly await this event, convinced as we are that the disillusionment of our Japanese colleagues is sure to follow. They very much over-estimate the importance of this article.

It would appear that in New York, reports of a different character have been received from Japan on the camphor monopoly. The information from there mentions already a rise in camphor and camphor products, and states at the same time that the most important Japanese factory of artificial sassafras oil (the well-known inferior product competing with safrol) has been closed. This report, given in the issue of 3<sup>rd</sup> March 1902 of the "Oil, Paint and Drug Reporter", says:

"The effect of the closing of this factory on the New York market is fully recognised. We are informed that on Monday a considerable rise in the price of artificial sassafras oil will take place, and it is not at all unreasonable to expect a further increase in the quotations with a decrease in the supply. If it is taken that the consumption of this article in the United States amounts to 300000 lbs. annually, the stocks would only be sufficient to meet the demand for about four months, and it is impossible to say what would then happen. If, as it would now appear to be the case, the supply becomes low, the values might rise so much that the use of the article will cease, for the soap manufacturers will be unable to employ it as soon as its value exceeds a certain limit."

We give this information without responsibility, and only for the sake of completeness, but may add that the journal in question is usually very well informed.

Until quite recently we have always given the specific gravity of safrol, at 15°, as 1.108, in accordance with a determination made years ago, and we have constantly judged the article on this basis. Im-

provements in the manufacturing process, however, which could not alter the safrol but might lead us to expect a product of greater purity, always yielded a somewhat lighter preparation.

This induced us to make a fresh determination of the specific gravity of safrol.

For this purpose we repeatedly re-crystallised safrol, purified by freezing and freed from water in vacuo, at first with the addition of about 10 per cent alcohol, and removed the mother liquor each time by centrifuge. The colourless, very hard crystals thus obtained melted at ordinary temperature to an absolutely limpid liquid, which, at  $15^{\circ}$ , had a specific gravity fluctuating between 1.1058 and 1.106 and, at  $17.5^{\circ}$ , an index of refraction  $n_D = 1.53917$ . The congealing point of this very pure safrol was found to be  $+ 11.2^{\circ}$ .

**Terpineol.** The consumption of this article appears to be still on the increase. In this case also great things are accomplished in the art of depressing the prices.

The current products show fairly large differences; for this reason it is necessary to keep a careful check on the physical constants. It should also be required of a good quality, that it is absolutely anhydrous.

**Thymol, cryst.** The prices of this important medicament have suffered great fluctuations, according as the owners of ajowan seed in India appeared more or less accommodating. In consequence of timely purchases we were able, during the critical period, to satisfy fully the demand from our regular clients.

At this moment cheap spring shipments are coming in, which enable us to make a further reduction in our selling prices. As operations in our new factory have now commenced, we shall in future be in a position to defy all fair competition.

The present value may be called normal. The quotations during 1901 show considerable differences. They were

in January . .	36	Marks	per kilo,
„ April . .	22	„	„ „
„ July . .	20	„	„ „
„ October . .	21	„	„ „
„ December .	20	„	„ „

whilst since the commencement of the present year they have gradually declined to 16 Marks.

We would avail ourselves of this opportunity to call attention to thymene, a by-product of the thymol manufacture, which we supply at very low rates, if ordered in large quantities. This product possesses prominent deodorising, and probably also antiseptic properties, and

renders excellent service in covering the tallow odour of common soaps for domestic use.

**Vanillin.** Continued improvements in the old manufacturing processes, and the discovery of new methods, have led to a further reduction in the cost price, accompanied by a general decline in the value. Where the conditions are so deplorable, the danger of adulteration is near at hand. Up to the present the following adulterants have been actually detected in the commercial article: acetisoeugenol, antifebrin, benzoic acid, sugar, and coumarin. A great number of examples have been described in detail in our previous Reports.

When we purchased vanillin for the first time in 1876, we paid £300 per kilo. At that time it was prepared from the fresh sap of the wood of conifers. With great trouble we were able to obtain in the course of several months about 500 grammes. In 1877 the price was about £100, in 1880 about £50, in 1890 about £20, in 1900 about £4 and two years later it stands at about £3 per kilo. Consequently, one can now purchase 100 kilos for the same amount which at the first appearance of the article was paid for 1 kilo.

As is well-known, the fruit of vanilla does not at the time of the harvest contain any vanillin; on the contrary, a special treatment is required, in the course of which the formation of vanillin takes place by a kind of fermentation process. The method of preparation which is in vogue in the vanilla-producing countries, such as Réunion, is purely empirical, and consists of immersing the fruit first for about 20 seconds in water of 80 to 85°, whereupon the aroma begins to develop. L. Lecomte<sup>1)</sup> now has discovered that the ferment which causes the fermentation belongs to the class of those bodies which after G. Bertrand are called oxydases. This oxydase is present in the most diverse parts of the vanilla plant, *Vanilla planifolia*, such as the leaves, twigs, ripe and unripe fruits. It is even found in the prepared vanilla, and that in greater abundance in the better qualities, from Mexico, Réunion, Mayotta and the Seychelles, than in those of less value, from Guadeloupe and Tahiti. It is further remarkable, that manganese, the never failing companion of oxydases, is also present in vanilla. The plant, however, contains a second ferment, which has a hydrolysing action, and which also plays a part in the process of fermentation.

The formation of vanillin would appear to occur in vanilla in this manner, that the hydrolysing ferment splits up the coniferin (which is

<sup>1)</sup> Compt. rend. 133 (1901), 745.

believed to be present) into coniferyl alcohol and glucose. The action of the oxydase would then oxidise the coniferyl alcohol into vanillin.

Lecomte proposes to make further experiments to test the correctness of this hypothesis.

Trillat<sup>1)</sup> obtained vanillin by passing air together with the vapours of isoeugenol over a red-hot spiral of platinum. The yield, however, was not large, and amounted only to 2.9 per cent of the isoeugenol experimented upon, part of the latter being recovered in the unaltered state.

**Schimmel & Co.**

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<sup>1)</sup> Compt. rend. **133** (1901), 822.

J. J. Weber, Leipzig.

SEMI-ANNUAL REPORT  
OF  
SCHIMMEL & Co.  
(FRITZSCHE BROTHERS)

MILTITZ

NEAR LEIPZIG

LONDON ☉ NEW YORK.



APRIL/MAY 1906.

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## List of abbreviations.

$d$  = specific gravity.

$d_{20^{\circ}}$  = specific gravity at  $20^{\circ}$ .

$d \frac{20^{\circ}}{4}$  = specific gravity at  $20^{\circ}$ , compared with water at  $4^{\circ}$ .

$\alpha_{D15^{\circ}}$  = optical rotation at  $15^{\circ}$ , in a 100 mm. tube.

$[\alpha]_D$  = specific rotation.

$n_{D15^{\circ}}$  = index of refraction at  $15^{\circ}$ .

$n$  = normal.

$\frac{n}{2} \left( \frac{n}{10} \right)$  = semi-normal or deci-normal (titrated solutions).

gm. = gram; cc. = cubic centimeter; mm. = millimeter.

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Temperatures are uniformly stated in **centigrade** degrees ( $^{\circ}$ ).

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In looking back on the year 1905, we can rejoice in the fact that the economic situation of Germany shows a further favourable development. The industrial activity was in part exceptionally animated, having largely recourse to the money market, — although the surprising increase of the bank-rate at the close of the year, as compared with the low rates at other of the world's principal exchanges, may perhaps have been due, not so much to a healthy development of industry, as to important financial engagements on the exchange, and speculative purchases of goods in view of the increases in the import-duties about to come into force. This state of extreme exertion gives food for thought, and may possibly lead to an increase in the resources of the Imperial Bank.

The new Tariffs naturally claimed the largest amount of interest. Since these Tariffs have become an established fact, each individual branch of industry will have to make for itself the best of the bargain.

In our own branch, the alterations are not of any very considerable importance. It is to be appreciated (because it adds to our capacity of competing with foreign countries), that after struggles lasting for many years, seeds for the production of essential oils are now at last to be admitted free, subject to official control, and the distillation-residues are likewise to be free, whilst at the same time the import-duty of these materials, in so far as they are used for other purposes, is raised from 3 to 4 marks per 100 kilos.

The duty on essential oils imported from Tariff countries (such as Italy, Russia, Bulgaria) has remained as hitherto at 20 marks, but for the other countries has been raised to 30 marks.

Vanillin, which up to now paid 50 marks duty, has been raised to 80 marks; oils of rosemary and juniper-berries have been advanced from 12 to 30 marks per 100 kilos. On the other hand, oils of turpentine, pine-needles, camphor, and juniper-tar (*ol. cadin.*) remain as before free of duty. We will return to the details when discussing the individual articles in the following pages.

In spite of the internal disturbances in Russia, our trade with that country was unusually brisk, to which the various alterations in the tariff also contributed. The importance of this market for our

products is clear from the fact that the total imports of essential oils in 1903 amounted to:

5436 poods, value 580984 roubles,  
 33 „ rose oil, value 83295 roubles,  
 of which from Germany:  
 2914 poods, value 312531 roubles,  
 10 „ rose oil, value 30260 roubles.

The principal alterations in the Russian tariff, which came into force on 1<sup>st</sup> March, are: essential oils, hitherto 24,— roubles plus 10%, now 26,40 roubles, according to treaty 16,80 roubles. Essences and fruit-ethers, hitherto 10,80 roubles, in future 25,— roubles, in bottles 30,— roubles. Extracts and pomades below 10 pounds from 13,60 to 52,50 roubles, according to treaty 36,75 roubles. Pomades in vessels containing at least 10 pounds, according to treaty 15,— roubles per pood gross. Vanillin, coumarin, heliotropin, from 2,25 to 24,— roubles, according to treaty 16,80 roubles. Nitrobenzene from 2,25 to 4,— roubles; menthol, thymol and similar chemical products not specially enumerated from 2,25 to 5,— roubles, according to treaty 4,— roubles per pood gross.

A unique case in the matter of tariffs is no doubt this, that according to the new treaty with Bulgaria, the import duty on essential oils, fruit-essences, and ethers, has been raised to 500 francs per 100 kilos, whilst Germany has agreed by treaty to a reduced tariff rate of 20 marks per 100 kilos for the importation of Bulgarian rose oil! The German Plenipotentiary has rendered a bad service to our Industry by agreeing to this.

The statistics for Austria show the following figures: —

Essential oils, imports in 1904:

124445 kilos, value 1700000 kronen;

Essential oils, exports in 1904:

73300 kilos, value 573550 kronen.

The alterations in the Tariff, as far as our specialities are concerned, are throughout unimportant, and are more for the purpose of rounding off. The oils of which the import duties were raised are Austrian products, and are of no importance for Germany.

The new tariff of Switzerland also brings but few important alterations. The import duty on camphor oil has been reduced from 2 to 1 franc. Safrol, which usually pays 45 francs, is admitted at 10 francs per 100 kilos on production of proof that it is to be used for the manufacture of heliotropin. Some essential oils, such as clove, lavender, spike, juniper, anise, lemon, peppermint, and cinnamon oils,

and further thymol, eucalyptol, and menthol, have been reduced to 8 francs per 100 kilos, whilst the remaining essential oils, in accordance with the treaty, are taxed as hitherto with 45 francs.

The sale of our products in the United Kingdom is growing, and the best possible relations with this important market have been maintained with the help of our London branch.

The imports of essential oils in the United Kingdom were in 1904:

1834421 lbs., value £ 265922,—,

of which from Germany:

107044 lbs., value £ 13824,—,

whilst the exports amounted to

602843 lbs., value £ 83339,—,

of which to Germany:

220922 lbs., value £ 28866,—.

The trade with the United States of North America was very brisk, in harmony with the economic growth of that country. In view of the equality of the mutual interests, it may confidently be expected that the tariff-difficulties, which have arisen may, be removed amicably while the provisional arrangement is in force, and that the result of the negotiations will be a treaty which will satisfy both parties and will be of long duration.

In spite of the critical situation in Japan, our commercial intercourse with that country was more animated than ever. It may be assumed that the new commercial treaty between Japan and China will also increase the purchasing power of the former country.

Of the South American states, Brazil still continues to suffer from the injurious effect of the fluctuating value of the exchange. The efforts made by the Government to bring about stability in the rate of exchange, must be looked upon as having failed. It is evident that the present state of affairs is not calculated to promote commercial intercourse. The prospects in the Argentine Republic are favourable; with a large increase in the immigration, this country is opened up more and more for civilisation, and its internal wealth also finds expression in the low rate of interest.

In Chile it has not yet been possible to carry out the intended introduction of the gold standard. The abundance of ready money, created by large issues of paper, has led to wild speculations, the rapid collapse of which has made numerous victims. Under these conditions a healthy increase in the exports to Chile is unfortunately out of the question.

The continued improvement in the economic situation in Spain finds expression in the uninterrupted rise of the exchange. In the opinion of leading interested parties, the premium on gold may possibly go back still further within the near future. The reform of the alcohol-law, which was almost hourly expected in the middle of December of last year, has been pushed in the background by other questions, and is now entirely in abeyance. The stormy manifestations of protest against this hated law, which in the course of a few months has totally ruined the wine-producers and the alcohol- and brandy-industries, have gradually died away, and the alcohol-question, which is of such importance for the whole country, has been postponed indefinitely.

Trade with France was very brisk on both sides. There can be no doubt that the negotiations at Algeciras having been concluded in a friendly spirit, in spite of a mischief-making press, they will form the basis of mutually satisfactory relations between France and Germany.

The intercourse with Italy was fairly lively. The favourable exchange has made this country a very desirable market.

The past six months show a preponderance of advancing quotations, which have also assisted in bringing about great animation in the trade during the first trimester of the current year, and which open up favourable prospects for the further course of 1906. The internal situation of our branch of industry is unchanged, and strict control is constantly required to prevent the honest trade from being strangled by corruption. In the following pages we endeavour, as usual, to deal with everything worth mentioning from a scientific and commercial point of view, and we hereby express the wish that it may be of interest and advantage to a number of our readers.

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## Commercial notes and scientific information on essential oils.

**Almond Oil, from apricot kernels.** The prices of Syrian kernels, which at the commencement of last harvest cost 64 francs, advanced a few francs in the course of the winter, and have kept at that level in consequence of a brisk demand. The selling prices of essential oil were firm, as the production was scarcely able to keep pace with the demand; the sale of pressed oil, however, was slow, at depressed prices. The use of almond oil for cosmetics (cold cream, etc.) appears to have fallen off, owing to the large number of vaseline and lanoline products; the competition of adulterated oils,

which are offered at incredible prices, also renders the sale of the genuine article more difficult.

**Almond Oil, pressed from sweet almonds.** Our quotations were adjusted in the late autumn in accordance with the cost-price of best quality 1905 Sicilian fruit. There are no grounds for any alteration in these quotations.

**Anise Oil.** The value of this important article has undergone further improvement since the date of our last Report, and it is probable that it will at least keep at its present level until the new anise-harvest. The same applies to anethol, the use of which for evident reasons is constantly acquiring larger dimensions. We carry on the manufacture of this product (which we were the first to introduce into commerce) on the largest scale, and in respect of quality supply the best that can possibly be attained, but we have been able to prove by numerous examinations, that inferior products are met with in commerce.

According to information received by us direct, a French firm in Bulgaria, which up to the present occupied itself exclusively with the distillation of rose oil, has now also taken up the distillation of Bulgarian anise, and hopes to produce this year a quantity of from 15000 to 20000 kilos anise oil. If this report is confirmed, a new competitor for Russia would here make his appearance.

The favour granted to our industry, to distil anise free from duty, will enable us in future to work up the various kinds of anise with advantage.

The German import of anise in the year 1904 was: —

in Stettin	from European Turkey	985 000 kilos
	„ the Netherlands	257 000 „
	„ Russia	36 000 „
	„ the German Customs Union <sup>1)</sup>	20 000 „
		<hr/> Total 1 298 000 kilos
in Hamburg	from the Russian Baltic ports	170 600 kilos
	„ Spain	21 600 „
	„ Turkey	112 100 „
		<hr/> Total 304 300 kilos.

Owing to the unfavourable state of the harvest, the import of anise in 1905 has declined considerably, for example, in Stettin it came to only 196 000 kilos; the figures of the import in Hamburg in 1905 have not yet come to hand.

<sup>1)</sup> Comprising the German Empire and the Grand Duchy of Luxembourg.

**Basil Oil.** The sources of this preparation which existed up to the present (France and Réunion) have recently become completely exhausted, and only inferior qualities are now met with in commerce. But it may be assumed that this scarcity will be relieved in the course of this summer. If the weather-conditions are favourable, we hope to produce some of this oil ourselves.

**Oil of Buchu Leaves.** With reference to some constituents, see page 119.

**Cajeput Oil.** The situation of this article is again normal, and does not give rise to any remarks except those of a statistical nature.

The shipments from Macassar during the year 1905 were as follows: —

to Europe . . . . .	312 piculs
„ America . . . . .	97 „
„ China . . . . .	163 „
„ Java . . . . .	1926 „
„ Singapore . . . . .	1437 „
<hr/>	
Total	3935 piculs

**Camphor Oil.** The peculiar situation of the camphor-market has also affected the oil. But so dark a veil lies over the whole, that at the present moment absolutely nothing can be said as to the future.

Such a large demand has arisen for the whole of the fractions which are formed as by-products in the manufacture of safrol, that we are quite unable to accumulate a stock and can only make firm offers (if at all) on receipt of special enquiries. The high prices of turpentine oil are no doubt the chief cause of the present state of affairs.

The quantity of camphor oil produced in Formosa was: —

in 1897	638603 kin <sup>1)</sup>
„ 1898	1120979 „
„ 1899	1369887 „
„ 1900	2362108 „
„ 1901	2587186 „
„ 1902	2388135 „
„ 1903	2690370 „
„ 1904	2730388 „

The production of camphor oil in Japan is decidedly smaller.

According to the official reports from the Imperial Japanese Ministry of Finance, camphor monopoly-offices have been established in Kagoshima, Nagasaki, Kennamoto, Fukuoka, and Kobe. These

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<sup>1)</sup> 1 kin = 1 $\frac{1}{8}$  lb.

offices have to deal with all matters concerning the production, collection, sale, and export of camphor and camphor oil, and also with the supervision of the camphor-monopoly.

In important places, sub-offices have also been established.

From the same source we quote the following export statistics of camphor:

	1898	1899	1900	1901	1902	1903	1904
	Yen <sup>1)</sup>	Yen	Yen	Yen	Yen	Yen	Yen
to Australia . . . .	5 650	12 284	47 724	32 904	43 067	50 442	26 272
„ British America . .	773	1 421	6 423	21 586	20 607	25 592	28 715
„ British India . . .	38 500	96 583	202 291	552 399	507 735	595 736	807 028
„ Straits Settlements	—	—	—	—	66 549	109 874	36 205
„ China . . . . .	1 787	9861	13 806	64 389	93 506	56 282	5 785
„ France . . . . .	1 972	257	29 510	183 722	33 050	360 275	693 569
„ Germany . . . . .	45 902	192 634	64 117	532 771	710 923	672 501	146 842
„ United Kingdom . .	35 568	29 490	429 412	949 723	800 288	491 047	79 026
„ Hong Kong . . . .	600 164	939 219	1 017 807	750 603	313 704	20 490	87 329
„ United States . . .	292 879	399 226	1 238 971	810 420	811 007	1 149 925	1 254 255
„ other countries . .	762	73 517	20 549	6 456	4 398	5 680	3 171
Totals	1 023 956	1 754 496	3 070 701	3 904 974	3 404 833	3 537 844	3 168 197

The year 1904 shows already a considerable falling off in the export<sup>2)</sup>, and this decrease may possibly have become much larger in 1905, if any conclusion can be drawn from the constantly advancing prices.

In discussing a pamphlet by Davidson<sup>3)</sup> on the camphor-industry in Formosa, it is stated in the *Journal d'Agriculture tropicale*<sup>4)</sup> that the camphor-trees in Formosa appear to be much richer than those in Japan. In the fertile damp soil of shady valleys, the trees contain less camphor than even on bad soil in open elevated situations. Trees rich in camphor are often found alongside trees with a very low camphor-content. The distribution of the camphor in the branches, trunk, and roots is unequal, and frequently more camphor is found in one particular side of the tree than in the other. Anyone specially interested in this question finds in Davidson's pamphlet information on the content of camphor and camphor oil in the various parts of the tree at different seasons, based on studies by Professor Moriga of Tokyo. The work does not, however, say anything on the cultivation of the camphor-tree. In Ceylon, where the leaves and twigs, gathered in the same way as tea, are distilled, the cultivation of the camphor-tree is said to be carried on extensively, but up to the present no large quantities of camphor have been exported from there.

<sup>1)</sup> 1 Yen = 2/-

<sup>2)</sup> See also Table on page 13.

<sup>3)</sup> L'Industrie du camphre à Formose. Imp. F. H. Schneider, Hanoy.

<sup>4)</sup> Journ. d'Agriculture tropicale 5 (1905), 351.

The United States Government had instructed its consuls in Japan and Formosa to supply reports on the camphor-industry of those countries, and received from its consul at Tamsui (Formosa) a comprehensive report, which represents a historical review of the camphor-industry since the introduction of the monopoly (August 1899), and, which, in addition to well known facts, also mentions interesting novelties, as we find from an article in *The Chemist and Druggist*.<sup>1)</sup>

The consul attributes the scarcity of crude camphor during the last two years to the fact, that in consequence of the Russo-Japanese war only a limited supply of labour was available in the forests; the cessation of hostilities had no doubt brought some improvement in the situation, but the consul, Mr. Fisher, does not believe that normal conditions will return until the end of 1906. The Formosa Government has engaged 2000 policemen and labourers to develop an area of 180 square miles with important camphor-forests in Northern Formosa; the Government also assists the opening up of districts in South Formosa. With regard to this, the shortage in the supply for the current year (1905) is estimated at 2400000 lbs., and for 1906 at 1000000 to 1500000 lbs.

The Japanese Government does not propose to raise the prices of crude camphor (although in case of urgent need it might be compelled to do so), in order not to stimulate still further the chemical research on the subject of the production of synthetic camphor. Whether synthetic camphor will be able to compete with the natural product when normal conditions again prevail in Japan and Formosa, is an open question. Manufacturers of celluloid will be interested to learn that it is reported that the manufacture of this article may ultimately be taken up in Japan.

With regard to the further state of affairs in Formosa, Fisher mentions that although the wages are very low, the transport of the crude material is extremely difficult. According to recent experiments, crude camphor can also be obtained from twigs and leaves, and it is the intention of the Monopoly-office to make use of this method as soon as the trees planted have reached their seventh year. Anyhow, the quantity of camphor produced in this manner will only form a small proportion of the total production.

The contract with the selling agents (Messrs. Samuel, Samuel & Co., London) runs until March 1906, and will probably be renewed. The scarcity of crude camphor exists since the end of 1903, and since that time the demand for crude camphor has been covered by immediate production, which this year was considerably lower. If no

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<sup>1)</sup> *Chemist and Druggist* **67** (1905), 975.

unforeseen circumstances occur, the prospects of a better supply of crude camphor are by no means hopeful.

The above information may be supplemented by means of a report on the same subject in the *Zeitschrift für angewandte Chemie*.<sup>1)</sup> According to this, the total production and export of crude camphor during the last five years was as follows: —

Year	Production in Formosa	Production in Japan	Manufacture at Kobe from camphor oil	Total production	Total export
	pounds	pounds	pounds	pounds	pounds
1900	4511184	2190175	—	6701359	6469220
1901	4725348	2669292	1635257	9029897	6717319
1902	3676060	3396908	1513795	8586763	9328399
1903	4071628	2948585	1613851	9354064	8965568
1904	4519923	900000	1979137	7399060	7372343

It is said that the Government now place three kinds of camphor on the market: „A“, refined camphor; „BB“, containing about 97 %; and „B“, about 95 per cent. To „A“ belong about 6 % of the export, and of the balance the „BB“ quality slightly exceeds the „B“. The American market is supplied almost exclusively with „B“ quality. In order to carry out the division of the stocks in hand at the different markets without partiality, the Government endeavours to allot the shipments to the individual countries according to their participation in the exports at the time when the Monopoly was established; this comes approximately as follows: Germany 37 %, America 33 %, France 15 %, the United Kingdom 10 % and India 5 %.

**Cananga Oil**<sup>2)</sup>. We have to record large sales in this oil. There are constantly direct shipments from Java on the way for us. At the present low prices this article is entitled to special attention.

**Caraway Oil.** The prices of caraway have on the whole suffered but slight fluctuations, so that there have been no grounds for any alteration in the prices of the oil.

It is a matter of importance for the industry which is here so highly developed, that our efforts to obtain freedom from duty for all so-called spice-seeds used for the distillation of essential oils, have at last been crowned with success. In connection therewith, the duty-free use of the residual seed for cattle-food has also been granted, and for this reason we may consider all danger past that our in-

<sup>1)</sup> Zeitschr. f. angew. Chem. **19** (1906), 261.

<sup>2)</sup> Report April, May **1905**, p. 19: read cocoa nut oil instead of “cocoa butter”.

dustry will be injuriously affected by the new duty, which has been raised from 3 to 4 marks.

Our clients will profit from the resulting advantage by a difference in the price of caraway oil of about 0,60 marks per kilo, to take effect from the coming season.

We avail ourselves of this opportunity to express our thanks to the Saxon Government, which has assisted to bring victory to our suggestions, and which has also regulated the practical execution of the customs' control in a most liberal and judicious manner.

We are now in possession of official reports on the results of the caraway-harvest in Holland in the year 1905, from which we see that the estimate of our Dutch correspondents published in our last October Report, was taken much too low. We reproduce below the figures published in No. 8 of the *Nederlandsch Landbouw Weekblad* of 24<sup>th</sup> February 1906; the figures in brackets are the results of 1904 added for comparison.

Provinces	Area under cultivation in acres		Yield in bales of 50 kilos	
			per acre	total
Groningen . . .	1 117	( 2 280)	8,8 (10,7)	9 864 ( 24 688)
Friesland . . .	65	( 117)	9,3 ( 9,8)	606 ( 1 147)
Drente . . .	52	—	5,4 —	282 —
Overijssel . . .	2 1/2	—	6,0 —	15 —
Utrecht . . .	30	( 45)	12,0 (14,0)	360 ( 630)
North Holland . .	4 512	( 5 237)	8,5 (10,5)	38 540 ( 54 911)
South Holland . .	512	( 660)	9,3 ( 9,4)	4 759 ( 6 191)
Zeeland . . .	2 070	( 2 505)	8,3 (11,1)	17 245 ( 27 798)
North Brabant . .	1 900	( 2 557)	7,8 ( 9,6)	14 801 ( 24 645)
Totals	10 260 1/2	(13 401)	8,4 (10,5)	86 472 (139 790)

On the prospects of this year's harvest, we are informed under date 6<sup>th</sup> March that in Brabant less caraway is under cultivation than in 1905, but that, on the other hand, the plants are in good condition and give great promise. The same applies to Zeeland. In North Holland, much land in the Ypold district had suffered greatly from mice; for this reason the yield will be much smaller than last year.

In the Haarlem district and in Groningen and Friesland, however, the area planted is not larger than in 1905, and the plants there are looking well.

It is hoped that the mild weather will now continue until the plants are sufficiently strong to resist subsequent night frosts, as the latter might otherwise do a great deal of harm.

The old stocks, which must be taken into consideration to form a correct opinion on the situation, are said to be distinctly low, but difficult to estimate.

According to the foregoing, low prices must not be reckoned upon in the coming season.

**Oil of Cardamine amara.** K. Feist<sup>1)</sup> has occupied himself with the examination of the essential oil of *Cardamine amara* L., a plant frequently confounded with *Nasturtium officinale* R. Br. The oil obtained by him by means of steam distillation of the pulverised fresh herb which had not yet blossomed, formed a brown liquid, with a pronounced water-cress odour. By the action of alcoholic ammonia a thio-urea was obtained from the oil, whose melting point (134 to 135°) and sulphur-content (mean 24,23%), correspond to those of the thio-urea obtained from secondary butyl isothiocyanate, — and, as might accordingly be expected, the body showed a feeble dextrorotation. The content of secondary butyl isothiocyanate in the fresh herb is given bei Feist as 0,0357%. Genuine water-cress, as is well known, contains phenyl ethyl-isothiocyanate.<sup>2)</sup> Secondary butyl isothiocyanate was first detected by A. W. Hofmann<sup>3)</sup> in the herb of *Cochlearia officinalis* L.

**Oil of Carline Thistle.** Semmler<sup>4)</sup> has again taken up his studies on the composition of the oil of Carline thistle (*Carlina acaulis* L.) which he commenced in 1889, and which has also formed the subject of an examination by Gadamer<sup>5)</sup>. The oil examined by Semmler had the specific gravity  $d_{19^{\circ}}$  1,0333, and the refraction  $n_D$  1,56960. He isolated from it 12 to 15% carlinene, a monocyclic sesquiterpene  $C_{15}H_{24}$  of the boiling point 139 to 141°, at 20 mm. pressure;  $d_{23,8^{\circ}}$  0,8733;  $n_D$  1,492. From the high-boiling portions of the oil, palmitic acid (melting point 62°) separated off. The principal constituent of oil of carline thistle is carlina oxide  $C_{13}H_{10}O$  (boiling point 167 to 168° at 20 mm. pressure;  $d_{17^{\circ}}^{17^{\circ}}$  1,066;  $n_D$  1,586;  $\alpha_D \pm 0^{\circ}$ ). Attempts made to determine the character of the oxygen atom led to no result. But on oxidation with potassium permanganate the body yielded large quantities of benzoic acid, and reduction with sodium and alcohol led to the tetrahydro compound  $C_{13}H_{14}O$ , which by means of oxidation with potassium permanganate gave the degradation product  $\gamma$ -phenyl butyric acid  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$  (melting point 52°).

<sup>1)</sup> Apotheker-Ztg. **20** (1905), 832.

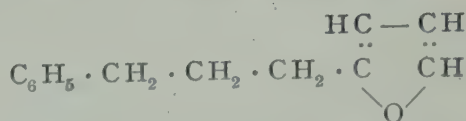
<sup>2)</sup> Arch. der Pharm. **237** (1899), 511.

<sup>3)</sup> Berl. Berichte **7** (1874), 513.

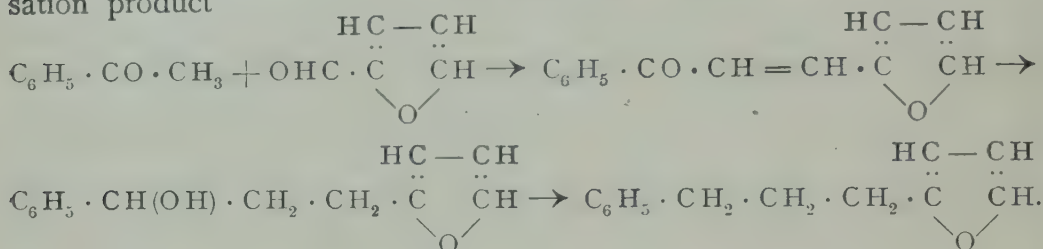
<sup>4)</sup> Berl. Berichte **39** (1906), 726.

<sup>5)</sup> Arch. der Pharm. **241** (1903), 44.

In the rest which had been oxidised away, Semmler suspected the furane ring, judging from the properties of the tetrahydro compound. The body  $C_{13}H_{14}O$  would then have been a 1-phenyl-3- $\alpha$ -furyl-propane



A synthesis of this compound made with that end in view confirmed the supposition, and proved the identity of the two bodies. It was accomplished by condensation of acetophenone and furfurol by means of potash liquor, and subsequent reduction of the condensation product



Now, if the last-named formula belongs to tetrahydro carlina oxide, the constitution



is very probable for carlina oxide. Semmler has commenced researches for the further elucidation of this question.

Owing to the fact that the principal constituent of oil of carline thistle is a furane derivative, the supposition hitherto accepted, that the furfurol of essential oils owes its origin to the decomposition of a compound belonging to the carbohydrates, must now in Semmler's opinion be narrowed down to this, that a portion of the furfurol may also be derived from compounds of the character of carlina oxide.

**Cassia Oil.** The prices for 80/85 per cent. oil, which in November still fluctuated between  $\frac{3}{7}$  and  $\frac{3}{8}$ , have gradually declined to  $\frac{3}{3}$  and have since remained at that level. We consider this a healthy value, and believe that a further drop is improbable. Oils of a lower content came cheaper on the usual scale. Unfortunately we had to observe repeatedly, and have also demonstrated, that middlemen had substituted oils of inferior aldehyde-content for the above highest-grade oil, which explained some remarkably cheap offers. We carry out aldehyde-determinations at all times free of charge, as it is our aim to keep the trade in this article, on which we have spent so much time and trouble, above suspicion.

**Cedarwood Oil (from Hayti).** A cedarwood oil sent over from Hayti, of whose botanical origin we were unable to ascertain anything more definite, but which according to the microscopical results was derived from a conifer, gave on distillation, in a yield of 4,33%, an oil of lemon-yellow colour and the odour of the common cedarwood obtained from *Juniperus virginiana* L. But it differs from the latter by its higher specific gravity ( $d_{15^\circ}$  0,9612), the lower rotation ( $\alpha_D$  —  $14^\circ 58'$ ), and the higher content of alcoholic constituents (ester number after acetylation 64,0). The acid number was 2,7, the ester number 5,0. The oil was not completely soluble in 10 vol. 90 per cent. alcohol, but dissolved in every proportion in 95 per cent. alcohol.

**Cinnamon Oil.** The sale of this article by our firm has acquired colossal dimensions, and appears to be still capable of further expansion. This result is no doubt due to the quality of our product. The price of fine Ceylon cinnamon-chips is practically unchanged. The figures of the export in 1905 again show a considerable increase.

They were: —

to Germany . . . . .	931 191 lbs.
„ the United Kingdom . . .	358 146 „
„ Belgium . . . . .	284 230 „
„ Italy . . . . .	169 344 „
„ Holland . . . . .	138 488 „
„ Spain . . . . .	102 260 „
„ America . . . . .	81 506 „
„ Australia . . . . .	72 398 „
„ Austria . . . . .	63 280 „
„ France . . . . .	20 404 „
„ Turkey . . . . .	8 960 „
„ Sweden . . . . .	1 400 „
„ India . . . . .	588 „

Total 2 235 395 lbs.

as against:

in 1904 . . . . .	2 135 220 lbs.
„ 1903 . . . . .	2 160 352 „
„ 1902 . . . . .	1 763 679 „

**Citronella Oil.** This important article has undergone fairly large movements during the last six months, and it would appear to us as if had acquired now, more than before, the character of an object of speculation, for the fact that the production has not fallen off is proved by the high figures of the export-statistics which closely approach those of the year 1902, but greatly exceed those of the last two years.

The shipments in 1905 from Colombo and Galle were: —

to the United States of America . . . . .	601 706 lbs.
„ the United Kingdom . . . . .	398 700 „
„ Germany . . . . .	193 331 „
„ Australia . . . . .	60 288 „
„ France . . . . .	11 925 „
„ China . . . . .	10 499 „
„ India . . . . .	3 645 „
„ Belgium . . . . .	2 161 „
„ the Straits Settlements . . . . .	2 16 „

Total in 1905 1 282 471 lbs.

as against:

„ 1904	1 133 068 „
„ 1903	1 027 486 „
„ 1902	1 294 750 „

On the other hand, the January shipments of a total of only 19618 lbs. show such an enormous falling off, as compared with a monthly average export of about 100000 lbs., that this fact appears to explain completely the lack of available goods and the high price of the same. It is only natural that this should influence forward deliveries, and the general situation will probably not become normal again until supply and demand have adjusted themselves to some extent. As already indicated above, speculators have aggravated the situation by buying up the available stocks in Europe, a step which could be carried out with a small amount of capital in view of the comparatively small quantities of oil.

In Ceylon, the distilling already came to an end in December, and as all the labourers are employed on the rice-fields in January, the work on the citronella grass-fields came for the time being completely to an end. Stocks are already cleared out, oil for early delivery is all contracted for, so that only later deliveries come under consideration. It is therefore possible that the position may become even more acute, and that the adjustment between supply and demand will only take place when stocks have again accumulated in the principal consuming countries.

We have been able, by placing our contracts in good time, to supply our clients fully, and we have also contracts running for April shipment which are shortly due.

Under these circumstances it is for the present out of the question that prices will go back, much less that the values formerly considered normal will again be reached.

C. E. Sage<sup>1)</sup> reports on a Ceylon citronella oil distilled at the Experimental Station established by the Government at Peradeniya

<sup>1)</sup> Chemist and Druggist 68 (1906), 355.

The examination of the dark orange-coloured oil gave the following results:  $d_{15,5^{\circ}} 0,884$ ,  $\alpha_D - 3,3^{\circ}$ , citronellal 36%, geraniol 41%; Schimmel's test: the oil gives with 80 per cent. alcohol only a cloudy solution. This inferior solubility of a guaranteed pure oil, induces Sage to attack Schimmel's test which, as is well known, consists of this, that citronella oil must form a clear solution with 1 to 2 vol. 80 per cent. alcohol at  $+20^{\circ}$ , remaining clear or showing at most feeble opalescence when up to 10 vol. solvent are added, from which even on prolonged standing no drops of oil must separate off. Sage designates this test an arbitrary determination, which no doubt may be useful in some cases, but which cannot give information on the quality of the oil; for the latter, only the content of geraniol and citronellal are decisive. For this reason it does not appear desirable, according to Sage, to retain Schimmel's test as a criterion for the purity of the oils.

In reply to this we would point out that we also have always supported and still support the view that for the quality of citronella oil the content of total geraniol (geraniol + citronellal) is above all decisive. But such determinations frequently take up too much time for commercial practice, and for this reason an easy and quickly completed method of testing was desirable, which should at least give general data as to the quality of the oils. Such a method Schimmel's test has proved to be; experience has shown that oils can be tested by it with good results, and it has been thoroughly acknowledged and recommended by leading experts. Mr. Sage's protest will affect it all the less, as the oil examined by him also differs so widely in its specific gravity and content of geraniol + citronellal from commercial Ceylon citronella oil<sup>1)</sup>, that a comparison with the latter appears out of place. To what cause these differences must be attributed is a matter which cannot be settled without further inquiry. What calls for particular attention is the fact that in spite of its high content of geraniol + citronellal (77%) the oil dissolves so badly. In the numerous commercial oils examined by us, we have always observed that the solubility of citronella oils increases with the content of total geraniol, and that consequently the solubility is most intimately related to the quality of the commercial oils. This fact has even induced us to introduce a "raised Schimmel's test", according to which citronella oil mixed with 5% Russian petroleum must show approximately the same solubility in 80 per cent alcohol as the original oil<sup>2)</sup>. We have no single instance observed that oils of superior quality have

<sup>1)</sup> Common commercial citronella oil has a specific gravity between 0,900 and 0,920 ( $15^{\circ}$ ) and a content of total geraniol (geraniol + citronellal) about 60%; in very few cases up to 70% has been observed.

<sup>2)</sup> Comp. Reports April 1904, 32; October 1904, 20.

not stood this test, and we can with full confidence recommend it to everyone interested in the honest trade in Ceylon citronella oil, notwithstanding the opposite view taken by Mr. Sage. We hoped that in this way may be accomplished that in course of time only the best quality Ceylon citronella oil is placed on the market.

**Clove Oil.** During the last six months this article has, along with the prices of cloves, been subject to very considerable fluctuations, for which really no sensible reason existed. Whoever examines the situation with some care, will come to the conclusion that it depends almost exclusively upon the speculators in India, London, and Holland, who have always shown a decided preference for this article; for even admitting that the last harvest has been below normal, it is equally certain that the one of 1904 has yielded an abnormally large quantity.

According to the following Report over 1904 from the German Consul at Zanzibar, the export of cloves was: —

	Pounds.	Value: Rupees.
in 1900 . . . . .	11788095	2372227
„ 1901 . . . . .	11962069	2465373
„ 1902 . . . . .	10125769	2057589
„ 1903 . . . . .	12092138	2795980
„ 1904 . . . . .	14502775	4986449

It was made up as follows: —

	1900	1901	1902	1903	1904
	Quantities in pounds.				
To Europe . . . . .	5235388	4470632	4160485	3551966	7312375
„ America . . . . .	719600	252000	412300	852361	2056175
„ Asia . . . . .	5769233	7081471	5412143	7560852	4839524
„ Africa . . . . .	63814	153966	140841	126959	94701

The shipments to America only went to New York, those to Asia to Bombay for the purpose of covering the Asiatic demand.

For the individual European markets, the exports were as follows: —

	1901	1902	1903	1904
	Quantities in pounds.			
to Rotterdam . . . . .	2330764	2210420	677618	1096860
„ London . . . . .	1841493	1295910	2014289	4779340
„ Hamburg . . . . .	125720	425015	465995	444995
„ Marseilles . . . . .	133000	188475	251664	251669

These figures show that Rotterdam has not succeeded in the last two years to carry through the attempt made to get the advantage over London.

Formerly the harvest-year was taken as the period from September to September. It is more correct to calculate it as August to August. The following figures give a review of the various harvest years since 1893: —

	from Zanzibar	from Pemba
	Quantities in frasihs <sup>1)</sup> .	
1893/1894 . . . . .	197710	402621
1894/1895 . . . . .	102208	307860
1895/1896 . . . . .	165901	413124

<sup>1)</sup> 1 frasihs = 35 lbs.

	from Zanzibar	from Pemba
	Quantities in frasilchs.	
1896/1897 . . . . .	84592	224362
1897/1898 . . . . .	44941	150703
1898/1899 . . . . .	149417	481565
1899/1900 . . . . .	59741	206640
1900/1901 . . . . .	37567	201192
1901/1902 . . . . .	43626	321599
1902/1903 . . . . .	175420	251780
1903/1904 . . . . .	28369	96792

From August 1904 to the end of April 1905, the following quantities were shipped: —

	from Zanzibar	from Pemba
	Quantities in frasilchs.	
1904. August . . . . .	7238	13094
September . . . . .	6143	71219
October . . . . .	4466	104308
November . . . . .	5679	80794
December . . . . .	6436	95689
1905. January . . . . .	9194	91024
February . . . . .	13655	51052
March . . . . .	9951	51433
April . . . . .	9746	30041

This shows a total quantity of 661162 frasilch for the period indicated. Up to August 1905, some 90000 frasilch will probably still be placed on the market. A crop of a total of about 750000 frasilch has not yet been recorded since the date when statistics were first kept.

The stocks of Zanzibar cloves are as follows: —

	in Holland	in London
End of 1904	3640 bales	27984 bales
„ „ 1905	6285 „	31390 „

These figures also show that Holland no longer possesses its previous importance as a clove-market, but on the contrary has been outstripped by London.

The present value of good marketable Zanzibar cloves is about 115 marks per 100 kilos, duty not paid. In view of the important part played by speculators in the determination of the value, any expression of opinion on the future of this article appears problematic.

We would still mention that the distillation of clove oil forms one of our specialities, and that for important contracts we are able to offer special advantages. The same applies to clove oil from stems.

Clove stems were shipped from Zanzibar

	in 1902	1903	1904
	Quantities in pounds.		
to Europe	2158642	1738468	1001665
Asia	177252	197321	145845
America	—	678178	86755

**Copaiba Balsam.** For the purpose of examining and estimating the value of copaiba balsam Utz<sup>1)</sup> recommends the determination of the index of refraction. He employed for his examinations a refractometer of Abbe's construction, and determined the refractive index at 15°. The values ascertained for commercial balsams derived from the most diverse sources lay between 1,5088 and 1,5258. Utz is not prepared to fix definite limits of value for the individual commercial qualities, as he had no authentic pure copaiba balsams at his disposal. An adulteration of the official balsam with gurjun balsam cannot be detected by the determination of the refraction, as the two balsams have approximately the same refractive power. An admixture of fatty oils and oil of turpentine, which possess considerably lower refractive indices, can, according to Utz, be detected by determining the refraction. The determination of the polarisation of copaiba balsam, which was carried out by Utz in a solution of carbon tetrachloride 1 : 5 did not afford any definite data for a valuation.

We would caution against attaching too great a value to the determination of the refractive index by itself: when it is a question of the detection of slight adulterations, this method will fail more readily than the usual one. The same applies to Rosenthaler's test, which appears useful to Utz in many cases. Rosenthaler<sup>2)</sup>, as is well known, uses a solution of vanillin in hydrochloric acid as reagent, and observes the colorations which occur with the balsams to be examined, both in the cold and when heated. As a violet coloration occurs both with pure copaiba balsam, and with gurjun balsam, which in the former case is feeble and disappears within a quarter of an hour, but in the latter is stronger and of longer duration, this method naturally fails where mixtures are examined.

**Copal Oils.** From a communication by L. Schmölling<sup>3)</sup> on copal oils, we abstract the following: — The most commonly used copals met with in commerce are Kauri and Manila copal, whose oils, separated from them by ordinary distillation, are employed for the manufacture of varnishes. The two kinds differ somewhat considerably in respect of content of resin acids, essential oil, etc. For further particulars we would refer to the work done by Wallach<sup>4)</sup> and Tschirch<sup>5)</sup>. Schmölling now has examined the essential oils of both resins, and from this it appears that they also show considerable differences. The Kauri oil is mobile, bright yellow, has a pleasant aromatic odour,

<sup>1)</sup> Apotheker-Ztg. **21** (1906), 72.

<sup>2)</sup> Zeitschr. f. anal. Chem. **44** (1905), 292. Report October 1905, 110.

<sup>3)</sup> Chem. Ztg. **29** (1905), 955.

<sup>4)</sup> Liebig's Annalen **271** (1892), 308.

<sup>5)</sup> Arch. d. Pharm. **239** (1901), 145; Report October 1901, 56. Arch. d. Pharm. **240** (1902), 202; Report October 1902, 31.

and does not change on exposure to the air.  $d_{15^\circ}$  0,8677; acid number 3,0; saponification number 4,9; iodine number 288,9. With the exception of petroleum ether, it dissolves in all solvents. On distillation the bulk of the oil passes over between  $150^\circ$  and  $160^\circ$ . When tested for pinene, Kauri oil yields an abundant quantity of crystals of nitrosochloride. It does not yield a solid addition product with bromine. The oil neutralised with semi-normal potash liquor is almost completely volatilisable with steam. Its portions boiling above  $170^\circ$  form with bromine in alcohol-ether solution a solid addition product, which points to the presence of limonene-like bodies.

The Manila oil distils over as a pink liquid which readily becomes cherry-red on exposure to the air, and which has the following properties:  $d_{15^\circ}$  0,9069; acid number 28,3; saponification number 45,7; iodine number 230,4. In all usual solvents, excepting petroleum ether, it dissolves completely. As distinguished from Kauri oil, only about 20% of the Manila oil distil over up to  $160^\circ$ , about 30% from  $160^\circ$  to  $185^\circ$ , and above  $250^\circ$  about 34%. With steam only about one half of the crude oil passes over. The bright yellow distillate has the specific gravity 0,8567; about 65% of it boil up to  $170^\circ$ . The author endeavoured without success to separate also from this oil derivatives of pinene and limonene. The distillation water of the Manila oil is rich in acids of which up to the present formic and acetic acids have been detected.

**Coriander Oil.** As during this season the Russian seed alone was obtainable, it was only natural that exceptionally high prices had to be asked for this oil, prices such as probably have never ruled before. In order to satisfy all demands addressed to us, we could not afford to let a single parcel of material go past us, yet we believe that our stock of oil will last until the new harvest.

**Oil of Cretian Origanum.** For a Sicilian oil, possibly derived from *Origanum creticum*, Umney and Bennett<sup>1)</sup> mention the following constants:  $d_{15^\circ}$  0,920°;  $n_D \pm 0^\circ$ ; phenol-content 44%, chiefly carvacrol; soluble in 2 vol. 80 per cent. alcohol, insoluble in 70 per cent. alcohol. 48% of the oil distilled over below  $220^\circ$ .

**Oil of Cryptomeria japonica.** K. Keimazu<sup>2)</sup> has detected in the essential oil of this conifer a dextro-sesquiterpene closely related to cadinene, which absorbs two molecules hydro-halogen, and contains two ethylene-linkings; he calls this body, whose physical constants differ from those of cadinene, cryptene. The oil contains further a polyatomic phenol, which yields a dibromine-product  $C_{11}H_{14}Br_2O_3$ .

<sup>1)</sup> Pharm. Journal **75** (1905) 860; Chemist and Druggist **67** (1905), 970.

<sup>2)</sup> Journ. of the Pharm. Soc. of Japan **1905**, 189. According to Pharm. Centralh. **46** (1905) 836. Comp. also Report October **1902**, 32.

**Dill Oil.** The cultivation of dill has increased considerably in Galicia last year, so that material for distillation is now available in abundance. The Galician seed yields an oil which is absolutely equal to that distilled from Thuringian seed.

According to the new German Tariff, dill seed has remained exempt from duty, although it really belongs to the same class as caraway, as it can also be used for alimentary purposes.

## Essential oils, Sicilian and Calabrian.

From the usual reliable source, Mr. Edoardo Jacob of Messina, we received the following valuable information on the essence market.

The statistics hereafter show that last year's export, as compared with that of the previous year, has suffered a falling off amounting to 137859 kilos, value 1048830 lire, or about 14%.

This reduction in the export is not, however, in any way due to a decline in the demand from abroad, but must be attributed to the fact that with the comparatively feeble crops of the winter-season 1904/1905, smaller quantities of oil were available for the export than in the preceding year. It has probably never happened before that the market has passed over from one season into another with stocks of all kinds of essences completely cleared out, as was the case in the autumn of 1905.

### Export of essential oils in the year 1905.

	1904		1905	
	kilos	lire	kilos	lire
a) from Messina:				
to North German ports . . .	21 220	318 300	20 227	323 632
„ Austria-Hungary . . .	73 825	1 107 375	78 128	1 250 048*)
„ Belgium . . .	3 778	56 670	3 239	51 824
„ Denmark . . .	2 666	39 990	3 894	62 304
„ France . . .	37 302	559 530	35 749	571 984
„ Greece . . .	616	9 240	545	8 720
„ the United Kingdom . . .	231 283	3 469 245	212 304	3 396 864
„ Holland . . .	11 013	165 195	8 818	141 088
„ Russia . . .	7 956	119 340	8 807	140 912
„ Scandinavia . . .	5 503	82 545	4 525	72 400
„ Spain and Portugal . . .	6 722	100 830	6 790	108 640
„ Turkey . . .	1 302	19 530	1 008	16 128
„ the United States . . .	389 378	5 840 670	307 692	4 923 072
„ South America . . .	—	—	—	—
„ Australia . . .	38 845	582 675	32 039	512 624
„ Egypt . . .	1 212	18 180	1 367	21 872
„ India . . .	1 295	19 425	768	12 288
„ other countries incl. Italy . .	14 436	216 540	16 667	266 672
Total	848 352	12 725 280	742 567	11 881 072

\*) In the exports to Austria-Hungary, the principal shipments to Germany are included, as these are sent out via Trieste.

	1904		1905	
	kilos	lire	kilos	lire
b) from Reggio:				
to North German ports . . . .	1 956	29 340	2 095	33 520
„ Austria-Hungary . . . .	28 558	428 370	19 614	313 828*)
„ France . . . .	20 564	328 460	21 765	348 240
„ the United Kingdom . . . .	25 146	334 295	36 789	588 624
„ Holland . . . .	3 111	46 665	1 210	19 360
„ the United States . . . .	23 011	300 150	11 941	191 056
„ other countries . . . .	2 396	35 940	1 905	30 480
Total	104 742	1 503 220	95 319	1 525 108

c) from Catania:				
to North German ports . . . .	360	3 600	460	4 600
„ Austria-Hungary . . . .	5 940	59 400	2 694	26 940*)
„ the United Kingdom . . . .	68	680	450	4 500
„ other countries . . . .	440	4 400	713	7 130
Total	6 808	68 080	4 317	43 170

d) from Palermo:				
to North German ports . . . .	24 10	24 100	1 583	15 830
„ Austria-Hungary . . . .	2 720	27 200	3 780	37 800*)
„ France . . . .	2 549	25 490	3 051	30 510
„ the United Kingdom . . . .	31 344	313 440	11 803	118 030
„ the United States . . . .	4 324	43 240	3 610	36 100
„ other countries . . . .	2 854	28 540	2 214	22 140
Total	46 201	462 010	26 041	260 410

Total exports:

	1904		1905	
	kilos	lire	kilos	lire
from Messina . . . .	848 352	12 725 280	742 567	11 881 072
„ Reggio . . . .	104 742	1 503 220	95 319	1 525 108
„ Catania . . . .	6 808	68 080	4 317	43 170
„ Palermo . . . .	46 201	462 010	26 041	260 410
Total	1 006 103	14 758 590	868 244	13 709 760

Summary of the export during the last 10 years.

Year	kilos	lire	Year	kilos	lire
1905	868 244	13 709 760	1900	842 246	10 972 295
1904	1 006 103	14 758 590	1899	797 145	10 722 445
1903	864 770	11 964 839	1898	667 293	9 015 083
1902	1 085 497	15 196 958	1897	732 092	9 719 133
1901	820 982	12 314 730	1896	514 067	7 579 424

\*) Comp. Note on page 24.

Whereas for lemons and oranges a good harvest is probable, too great expectations should not be entertained for a rich bergamot-harvest, as the tree has lost much strength owing to the last abundant crop and the high oil-content of the fruit, and is in need of rest and recovery.

With regard to the individual kinds of essences, the following is mentioned: —

**Bergamot Oil.** In the autumn of 1905, there was a very satisfactory prospect of a good medium harvest, whilst the stocks of prompt oil had dwindled down very much; when in the course of October a brisk demand came from abroad for spot oil, the orders could only be executed at advancing prices, so that this article from 18,50 marks at the beginning of September, rose in the course of October and the first half of November to 21 marks. But the small stocks of old oil were not sufficient to satisfy the sudden demand from abroad, and as a consequence the new oils, in spite of their usual low ester-content of 30 to 31<sup>0</sup>/<sub>0</sub>, were taken from the market at full prices, and at first fetched the same prices as old finest quality oil.

This, however, only lasted until more abundant supplies were placed on the market; as soon as this was the case, the article fell back to more sensible quotations.

Declining slowly, they reached about the middle of December their lowest level of 17,75 marks, to advance again in the last few days of December to 18,25 marks, owing to a more brisk demand. At this level the prices kept during the first month of the new year, and only dropped a little again in February.

If it is considered that the manufacturers have had at their disposal a good medium crop of fruit, and that moreover the fruit has given a rich yield of oil, it would not seem probable that the price of this article could be kept at the present level; but there is every indication that the opposite will be the case.

In spite of the much richer harvest, the present stocks, owing to the continued brisk export, are only very little larger than in the previous year, and there are probably at present smaller stocks of oil held abroad than in March of last year.

If it is further taken into consideration that the bergamot-tree only on the rarest occasions gives two good crops one after the other, the conclusion will be drawn that the prices of bergamot oil in the course of the next six months will hardly go lower, but that, on the contrary, it is not improbable that the summer and autumn will bring a slow upward movement in the value of this article.

**Lemon Oil.** The trade in lemon oil was so animated during the autumn months of last year, that the market, contrary to the view

expressed in the autumn Report, had completely disposed of its stocks of old oil before the new harvest commenced, and for this reason the new oil was able to make its appearance under the most favourable circumstances.

The old oils, in the course of October and November, fetched on the average 5 marks per kilo, and the less valuable new oil could at first not be sold at this figure, but the demand for new oil from all quarters soon became so violent that its value rose already in the middle of December to 5,10 marks, and has since advanced gradually to 5,80 marks per kilo cif. Trieste.

This movement has been promoted by various circumstances, for example, right at the commencement of the harvest by the exceptionally bad weather which prevailed in Sicily during December and January. Especially in the first half of December, continued rains greatly interfered with the work in the lemon-gardens and with the gathering of the fruit, and caused a considerable restriction in the manufacture. It is moreover obvious that the lack of old oil and the brisk demand from abroad have supplied a further lever for raising the prices; but, finally, the most particularly stubborn resistance of the manufacturers should be mentioned who, contrary to their usual habit, endeavoured to keep the market short of oil, and who thereby succeeded in obtaining the result favourable to their interests.

Since the formation of the Union of Manufacturers, to which reference has already been made on various occasions, the market must be gauged with a different measure than hitherto. Several bad harvest years following one another, and a hare-brained competition among the manufacturers, had brought this class to the verge of destitution. The natural consequence was that they were unable to hold back their products, essence and citrate of lime, but had to turn them immediately into hard cash in order to pay their workmen.

When last year the common distress had finally brought all the manufacturers together, the consequences of a regular supply corresponding to the demand immediately made themselves felt at Messina, and although the people in their excess of zeal took some false steps which finally turned out to their disadvantage, the net result of the combination was excellent for every individual member. Old debts had been paid, and everyone had a larger or smaller balance of cash in hand, so that for the new harvest the people were less dependent upon credit and upon raising money by contracts for forward delivery.

It will readily be understood that under these circumstances forward business became very difficult for the export firms, and for this reason it is all the more incomprehensible that a large Messina firm entered rashly into engagements with buyers abroad for enormous quantities of new oil at exceedingly low prices.

Such proceedings could not fail to become known or to attract observation in Messina, and the Manufacturers' Union found therein a desired opportunity to promote its own interests, by manipulating the supplies in the most skilful manner. The Union which — as already mentioned — was also greatly favoured by the weather-conditions, succeeded in keeping the market in hand, and controlling it according to its own views, so that the article under these conditions has slowly but continuously advanced from 4,75 to 5,80 marks, and has maintained itself at that level.

The conditions affecting the production, which come under consideration, now appear as follows: —

The quantity of lemons available for manufacture may be more or less equal to that of the previous year, but it appears questionable whether the quantity of oil produced from it will meet with the world's consumption. It is a fact that the approximately equal quantity derived from the crop of the winter of 1904/05 has not satisfied the demand, for the latter has used up during last year not only the entire new production of oil, but also the stocks of old oil still on hand in November 1904 both here and abroad. Although it may on the other hand be assumed that the high prices will bring about a reduction in the consumption of lemon oil, this would only dispose of the argument of prices higher than the present ones, whilst a drop in the prices before the appearance of the new harvest in November is not probable.

Two hitherto uncertain factors in these suppositions are, on the one hand the steps which the manufacturers may take in the future, and on the other, the prospects of the coming harvest. The former will constantly endeavour to push up the prices of the article, the latter may be in a greater or lesser degree favourable towards such endeavours, or they may thwart them.

With regard to the prospects of the harvest of the current year, it is at this moment impossible even to express any conjectures. The unusually large quantity of rain which has fallen during the last three months and the quiet atmospheric conditions have supplied an abundance of strength to the trees and prevented the excessive dropping of the leaves; it is therefore probable that all citrus species will blossom very abundantly. But the formation and development of the young fruit will depend entirely upon the weather prevailing in April, May and June.

**Mandarin Oil.** The mandarin-tree is the only one of our *citrus* species which has given a full crop in the harvest period. The fruit was very fine, well developed, and of excellent keeping qualities that is to say exceedingly suitable for export. This has largely interfered with the manufacture of oil, and although occasionally favourable opportunities for purchase have offered themselves in this article when

superior qualities could be bought at low prices, the prices have rapidly hardened, and have gradually risen to 34 to 35 marks.

**Orange Oil, bitter.** The bitter orange-tree has also suffered from the frosts of the winter of last year, and has consequently produced a bad crop. The prices of this fruit also kept very high, and oil of bitter orange could only be manufactured on a limited scale.

Under these circumstances the prices of the oil set in at a very high level and rapidly advanced to 17 marks, at which figure they have since kept for faultless first-class goods.

**Orange Oil, sweet.** The fear expressed in our autumn Report that the new crop would prove to be a poor one, and that the new season's manufacture would only find a very limited working sphere for a remunerative yield, has been confirmed to an almost unexpected extent.

Whilst the orange-crop generally had been marked out already as a very feeble one by the injurious effect of last winter's frosts, the position of the oil manufacture especially has been extremely difficult.

In the course of the summer already the oranges at the growers' fetched prices which appeared to put the advantageous use for oil manufacture out of the question, and these prices have as a matter of fact continued in force until the very last, as with the feeble crop equal to not more than half of that of the previous year, the fresh fruit for shipment in boxes as well as for railway traffic in bulk, constantly found a ready sale at advancing quotations. As the oil manufacturer could not afford to pay such prices, there naturally followed an unusual drop in the oil manufacture, and in the present season hardly 40 % of the previous year's oil has been produced.

The prices of old oil moved during the autumn between 13,75 and 14,— marks; the new oil at once found purchasers at the same prices, and then gradually rose in October and November to 17 marks. Early in December the upward movement weakened, and a slight drop occurred; but already in the middle of that month a fresh demand sprang up, and with it a recurrence of the upward movement, which brought the article at the close of the year to 17,75 marks.

With a slow but certain advance orange oil has meanwhile arrived at 18,25 marks, and to all appearances a further considerable increase in the value is to be expected before the new harvest.

The visible stocks can at present amount to at most 5000 kilos, against 12000 kilos at the same time last year; and this small quantity has not only to meet the further demand from abroad, but also to cover the shortage existing at Messina.

**Estragon Oil.** Our stock is very nearly exhausted, only a very small quantity being in hand; but the herb planted out in our fields here will enable us to distil a large quantity of oil during the coming season.

**Eucalyptus Oil.** Our sales of the distillate of the *Globulus* species have last year acquired very large dimensions. The required quantity was supplied chiefly by Australia, Algeria only supplying a small portion. No alterations in the price can be recorded.

Since our last Report we also received a direct consignment of oil of *Eucalyptus maculata* var. *citriodora*, which had long been absent, and which has now again been included in our lists. The oil owes its beautiful balmlike odour to its principal constituent, citronellal.

According to comparative tests made by R. C. Jackson<sup>1)</sup> with regard to the distillation of the oils of *Eucalyptus oleosa* and *Eucalyptus Globulus*, the leaves of the second year's growth of *E. oleosa* contain the largest quantity of oil; next in order come those of the second year of *E. Globulus*, then those of the first year of *E. oleosa*, and finally those of the first year's growth of *E. Globulus*. Phellandrene could only be detected in the oil of *E. oleosa*.

According to Jackson, the Smithson Development Co. of San Rafael, Cal., works up daily 8 tons eucalyptus leaves, which are distilled with steam under pressure.

Baker and Smith<sup>2)</sup>, who have already supplied many contributions to the chapter of Eucalypts, again give information on several West-Australian species. We only deal with this work in so far as it affects the essential oils, and would refer to the original for the botanical description of the various species.

We would make the preliminary remark, that Baker and Smith here again lay stress on the close relations which in their opinion exist between the botanical character of the eucalyptus species, and the chemical constituents of the essential oils contained in them. They specially return to this point, because the statement made by them several years ago in another place<sup>3)</sup> that the oil of *E. calophylla*, according to the nervature of the leaf, should contain much pinene and no phellandrene, has been confirmed by the examination now made.

1. Oil of *Eucalyptus calophylla* R. Br. (Red Gum). The oil, obtained in a yield of 0,248%, had a dark-red colour and a turpentine-

<sup>1)</sup> Amer. Soap Journ. 16 (1905), 74. Accord. to Chem. Ztg. Report. 30 (1906), 37.

<sup>2)</sup> Pharm. Journal 75 (1905), 356, 382.

<sup>3)</sup> Journ. and Proceed. of the Royal Soc. of N. S. W. vol. 35 (1901). Report April 1902, 41.

like odour;  $d_{15}^{\circ}$  0,8756;  $\alpha_D + 22,9^{\circ}$ ; saponification number 10,51; does not form a clear solution in 10 vol. 80 per cent. alcohol. The oil consists chiefly of d-pinene, and further contains cymene, sesquiterpenes, and small quantities of acetic esters. Traces of cineol only could be detected in the portions of the oil boiling about  $176^{\circ}$ ; phellandrene, aromadendral and piperitone were entirely absent. The dark colour of the oil disappeared rapidly on shaking with dilute soda solution.

2. Oil of *Eucalyptus diversicolor* F. v. M. (Karri). Yield 0,825%. The crude oil had a bright lemon-yellow colour, and a turpentine-like odour, and dissolved in 1 vol. 80 per cent. alcohol;  $d_{15}^{\circ}$  0,9145;  $\alpha_D + 30,1^{\circ}$ ; saponification number 53,2. A preliminary examination showed that the oil consisted chiefly of d-pinene; it also contained small quantities of cineol (less than 5% in the fraction boiling between  $172$  and  $181^{\circ}$ ) and about 20% of an acetic acid ester. Phellandrene could not be detected in it.

3. Oil of *Eucalyptus salmonophloia* F. v. M. (Salmon Bark Gum). The yield of oil amounted to 1,44%. The crude oil had a reddish colour, and had an odour of pinene and at the same time eucalyptol; it had also a faint secondary odour of aromadendral;  $d_{15}^{\circ}$  0,9076 ( $d_{15}^{\circ}$  of the rectified oil 0,9052);  $\alpha_D + 6,3^{\circ}$ ; saponification number 4,97; soluble in 3,5 vol. 70 per cent. alcohol. Constituents of this oil are chiefly pinene and eucalyptol (about 50%) and further small quantities of aromadendral. Phellandrene was not present.

4. Oil of *Eucalyptus redunca* Schauer (White Gum or Wandoo of Western Australia). The oil obtained in a yield of 1,205% had in the crude state a red colour; when rectified it was almost colourless. The odour of pinene predominated, besides it had the odour of eucalyptol. The remaining properties of the crude oil were:  $d_{15}^{\circ}$  0,9097;  $\alpha_D + 13,5^{\circ}$ ; saponification number 2,4. The oil only dissolved in 6 vol. 70 per cent. alcohol, which must be attributed to the high content of d-pinene. There were further found eucalyptol in a quantity of about 40%, and traces of esters, whilst the higher-boiling portions (about 3%) consisted of sesquiterpene. The test for phellandrene gave negative results. At the same time leaves of young plants ("suckers") of this eucalyptus species were distilled, and the oil thereby obtained was found identical with the one described above.

5. Oil of *Eucalyptus occidentalis* Endl. (Mallet Gum). Yield 0,954%, colour and odour the same as of the previous oil;  $d_{15}^{\circ}$  0,9135;  $\alpha_D + 9^{\circ}$ ; saponification number 2,48; soluble in 1 vol. 80 per cent. alcohol. The composition is similar to that of *E. redunca*; it is only a little richer in sesquiterpene and also contains small quantities of aromadendral.

6. Oil of *Eucalyptus marginata* Sm. (Jarrah). The yield of oil differed according as the leaves used were those of old trees or of

young ones ("suckers"); in the former case 0,243% were obtained, in the latter only 0,198%. It should also be taken into consideration that the material was derived from different districts. In spite of this, the properties and composition of the two oils were on the whole the same, with the exception that the oil obtained from "suckers" was richer in terpenes and consequently of less specific gravity and also more difficult to dissolve.

Oil from older leaves:  $d_{15^\circ}$  0,9117;  $n_D$  — 8,5°; saponification number 13,1; soluble in 1 vol. 80 per cent. alcohol.

Oil from leaves of "suckers":  $d_{15^\circ}$  0,8889;  $n_D$  — 10,4°; saponification number 10,25; soluble in 5 vol. 80 per cent. alcohol.

The crude oils had a red colour, and the odour of aromadendral. The following constituents were detected: cymene, aromadendral, small quantities of pinene and eucalyptol, further geraniol (?) in the form of the acetic ester. Phellandrene was not present.

7. Oil of *Eucalyptus gomphocephala* D. C. (Touart or Tooart). The oil obtained in a yield of only 0,031%, had a reddish colour and a rancid disagreeable odour, which reminded little of that of ordinary eucalyptus oils. It consists chiefly of terpenes, among which in abundance phellandrene, and is consequently difficult to dissolve; even with 10 vol. 80 per cent. alcohol no clear solution could be obtained. Cineol could not be detected, but an acetic acid ester was found to be present;  $d_{15^\circ}$  0,8759; saponification number 25,74.

8. Oil of *Eucalyptus salubris* F. v. M. (Gimlet Gum). The distillation gave a yield of 1,391% oil, which in the crude state had an orange to reddish brown colour, and a powerful aromadendral odour.  $d_{15^\circ}$  0,902;  $n_D$  — 5,8°; saponification number 18,88. In 10 vol. 70 per cent. alcohol the oil was insoluble, but it dissolved in 1 vol. 80 per cent. alcohol. It is fairly rich in high-boiling constituents, as only 66% passed over below 183°. In the fraction passing over above 214°, aromadendral was present in abundant quantity. There were further found in this oil: d-pinene, cymene, eucalyptol (about 10%), and esters which probably consisted chiefly of geranyl acetate.

The comparatively high content of aromadendral of the oil of *E. salubris*, induced Baker and Smith to once more submit this aldehyde to a thorough study. It was then found, in agreement with previous results<sup>1)</sup>, that it is really a new aldehyde, contrary to the observation which we again made recently<sup>2)</sup>, according to which the aldehyde with a cuminal odour which we detected in several oils, is identical with cuminal aldehyde. From this it must be concluded that two different aldehydes possessing the same odour are present in the various eucalyptus oils, of which one is cuminal aldehyde.

<sup>1)</sup> Report April 1901, 33; October 1901, 29.

<sup>2)</sup> Report October 1903, 36.

For the purpose of isolating the aldehyde, which process was carried out in the usual manner with the help of the bisulphite compound, Baker and Smith used the portions of the oil boiling above  $190^{\circ}$ . The yield of aromadendral was 1,6%. The pure aldehyde is a bright yellow mobile liquid, with a peculiar odour;  $d_{22^{\circ}} 0,95325$ ;  $n_{D22^{\circ}} -86,2^{\circ}$ ;  $[\alpha]_{D22^{\circ}} -90,43^{\circ}$ ; boiling point  $218$  to  $219^{\circ}$  with partial decomposition. Of derivatives there were produced, the oxime (melting point  $86^{\circ}$ ), the hydrazone (melting point  $104$  to  $105^{\circ}$ , when prepared in acetic solution; the hydrazone prepared in solution of alcohol or petroleum ether melted slightly higher, but was less stable), the naphthocinchoninic acid (melting point  $245$  to  $246^{\circ}$ ). Combustions gave figures corresponding with the formula  $C_9H_{12}O$ .

The compound readily absorbs bromine with formation of a liquid dibromide ( $d_{22^{\circ}} 1,4302$ ), which on being heated splits off hydrobromic acid, when probably a monobromide remains behind. From the high specific gravity, the high refractive index, and the other behaviour, it may be concluded that the aldehyde represents a cyclic compound. The molecular refraction calculated from  $d_{16^{\circ}} 0,9576$  and  $n_{D16^{\circ}} 1,5141$ , according to Lorenz-Lorentz, is 42,76; for  $C_9H_{12}O$ , the result (assuming 3 double linkings) is 42,529.

By oxidation with potassium bichromate and sulphuric acid, aromadendral was converted into an unsaturated monobasic acid (aromadendrinic acid,  $C_9H_{12}O_2$ ). The acid dried at  $105$  to  $110^{\circ}$ , melted between  $137$  and  $138^{\circ}$ , when simultaneously a slight sublimation could be observed; the air-dry crystals, however, melted at a lower temperature, but had no constant melting point. The acid is almost insoluble in cold, slightly soluble in hot water, but dissolves readily in alcohol and ether. Combustion, and determination of molecular weight and of silver of the silver salt, gave values corresponding to the formula  $C_9H_{12}O_2$ . The oxidation products of aromadendral are to be examined still further later on, chiefly with the view of solving the problem of the structure of aromadendral.

The observation that the aldehydes isolated from the various eucalyptus oils showed strongly divergent rotations, led Baker and Smith to the view that aromadendral occurs in both optical modifications, which also appears to follow from the similarity of the oximes, hydrazones and naphthocinchoninic acids of the differently rotating aromadendrals. On the other hand the authors consider it also possible that in a few cases, as for example in that of oil of *E. hemiphloia*, cuminic aldehyde is present, which for the rest is undoubtedly the case in accordance with our above-mentioned examinations.

In a work which may be taken to represent a supplement to R. T. Baker and H. G. Smith's work "A research on the Eucalypts,

especially in regard to their essential oils<sup>1)</sup> H. G. Smith<sup>2)</sup> gives the indices of refraction and a few other properties of 118 authentic eucalyptus oils, which with few exceptions had been distilled at the Technological Museum of Sydney from leaves of which the botanical origin had been determined by Baker. Smith determined the refractive indices, specific gravities, and solubilities of the oils in 70 per cent. ( $d_{15,5^\circ} 0,8722$ ) alcohol at  $16^\circ$ , and calculates, apart from the specific refractive power, for the oils rich in eucalyptol, numbers which appear to him useful for valuing the quality of the oils, by multiplying the value of the refractive index with ten times the value of the vol. 70 per cent. alcohol required for dissolving 1 vol. oil. The oils richest in eucalyptol make the best solutions with 70 per cent. alcohol, and have the smallest index of refraction, so that they stand at the top of the series arranged by Smith; it is clear from the numbers given, that the simple determination of the solubility by itself is at least of equal value, if not more valuable, than this new and more complicated method. Smith arranges his results in tables corresponding to the compositions of the oils.

The first group consists of oils rich in eucalyptol containing pinene, and usually free from phellandrene, whose refractive index was chiefly found above 1,47 and below 1,48. To these belong:

*E. amygdalina*, *E. Behriana*, *E. bicolor*, *E. Bosistoana*, *E. Bridgesiana*, *E. Cambagei*, *E. camphora*, *E. cinerea*, *E. cneorifolia*, *E. conica*, *E. cordata*, *E. dealbata*, *E. dumosa*, *E. eugenioides*, *E. Globulus*, *E. goniocalyx*, *E. gracilis*, *E. hemilampra*, *E. intertexta*, *E. longifolia*, *E. maculosa*, *E. Maidenii*, *E. melliodora*, *E. microcorys*, *E. Morrisi*, *E. occidentalis*, *E. odorata*, *E. oleosa*, *E. ovalifolia* v. *lanceolata*, *E. paludosa*, *E. pendula*, *E. polyanthema*, *E. polybractea*, *E. populifolia*, *E. propinqua*, *E. pulverulenta*, *E. punctata*, *E. quadrangulata*, *E. redunca*, *E. resinifera*, *E. Risdoni*, *E. Rossii*, *E. rostrata* var. *borealis*, *E. salmonophloia*, *E. Seeana*, *E. sideroxylon*, *E. Smithii*, *E. squamosa*, *E. stricta*, *E. Stuartiana*, *E. viminalis* var.

In the second group are found oils free from phellandrene, containing pinene, whose refractive index lies above 1,47 and below 1,48. These are the oils of *E. botryoides*, *E. calophylla*, *E. dextropinea*, *E. diversicolor*, *E. laevopinea*, *E. saligna*, *E. Wilkinsoniana*.

To the oils of the third group, free from phellandrene, containing pinene and sesquiterpene ( $n_{D16^\circ}$  above 1,48) belong the oils of *E. affinis*, *E. apiculata*, *E. Baeuerleni*, *E. corymbosa*, *E. eximia*, *E. intermedia*, *E. lactea*, *E. maculata*, *E. nova-anglica*, *E. paniculata*, *E. patentinervis*, *E. rubida*, *E. tessellaris*, *E. trachyphloia*.

<sup>1)</sup> Sydney 1902. Comp. Report April 1903, 40.

<sup>2)</sup> According to reprint kindly sent to us. Journ. and Proceed. of the Royal Soc. of N. S. Wales 39 (1905).

The fourth group is formed by the oils containing aromadendral, free from phellandrene ( $n_{D16}^{\circ}$  above 1,48) of *E. albens*, *E. hemiphloia*, *E. marginata*, *E. punctata* var. *didyma*, *E. rostrata*, *E. salubris*, *E. tereticornis*, *E. viridis*, *E. Woollsiana*.

Oils of the fifth group containing phellandrene and piperitone ( $n_{D16}^{\circ}$  above 1,48, frequently above 1,49) are those of *E. coriacea*, *E. delegatensis*, *E. dives*, *E. fraxinoides*, *E. Luehmanniana*, *E. obliqua*, *E. oreades*, *E. piperita*, *E. radiata*, *E. Sieberiana*, *E. vitrea*.

In the sixth group the oils containing phellandrene and sesquiterpene are given, whose refractive index lies above 1,48, and in some cases above 1,50. Here we find *E. acmenoides*, *E. angophoroides*, *E. capitellata*, *E. crebra*, *E. Dawsoni*, *E. fastigata*, *E. Fletcheri*, *E. gomphocephala*, *E. haemastoma*, *E. macrorrhyncha*, *E. melanophloia*, *E. microtheca*, *E. nigra*, *E. ovalifolia*, *E. Planchoniana*, *E. pilularis*, *E. robusta*, *E. siderophloia*, *E. sideroxylon* v. *pallens*, *E. stellulata*, *E. viminalis*, *E. virgata*.

The last, seventh group, includes the other not classified oils, which contain geraniol, geranyl acetate, citral, citronellal, etc. To this belong the oils of *E. citriodora*, *E. Macarthuri*, *E. Staigeriana*, and *E. aggregata*.

Of the excellent work "A critical revision of the genus *Eucalyptus*" by J. H. Maiden, to which we have already repeatedly referred in our Reports<sup>1)</sup>, we have now before us the seventh part<sup>2)</sup>, to which are appended four plates with illustrations. This part contains a detailed discussion of the following species: —

1. *Eucalyptus regnans* F. v. M. [Syn.: *E. amygdalina* Labill. var. *regnans* F. v. M., *E. amygdalina* Labill. var. *colossea* F. v. M., *E. inophloia* F. v. M., *E. fastigata* Deane et Maiden].
2. *Eucalyptus vitellina* Naudin and *E. vitrea* R. T. Baker.
3. *Eucalyptus dives* Schauer [Syn.: *E. amygdalina* Labill. var. *dives* F. v. M., *E. amygdalina* Labill. var. *latifolia* Deane et Maiden].
4. *Eucalyptus Andrewsii* Maiden [Syn.: *Sieberiana* F. v. M. var. *Oxleyensis* Deane et Maiden].
5. *Eucalyptus diversifolia* Bonpland [Syn.: *E. santalifolia* F. v. M., *E. dumosa* Benth. non A. Cunn., *E. cneorifolia* D. C. (partim) (?), *E. connata* Dum.-Cours., *E. santalifolia* F. v. M. var. *firma* Miq., *E. firma* F. v. M. herb. ex Miq., *E. cuspidata* Tausch, *E. viminalis* Labill. var. *diversifolia* Benth., *E. pachyloma* Benth.].

**Oil of European Pennyroyal.** There is at this moment a scarcity of this oil, as failure of the harvest has taken place both in

<sup>1)</sup> Report October 1903, 38, October 1904, 39, April 1905, 37, and October 1905, 33.

<sup>2)</sup> Sydney 1905.

Spain and in Algeria, and the small quantities produced have already been used up. Consumers of large quantities will therefore have to comfort themselves with hope for the coming autumn.

Since some time endeavours are also being made in Sicily to cultivate European pennyroyal (*Mentha pulegium*). Hitherto the distilling experiments were entirely confined to plants growing wild. Such an oil has been examined by Umney and Bennett<sup>1</sup>). The oil, which in odour and appearance did not differ from the ordinary French or Spanish oil, was probably also derived from *Mentha pulegium*, but in its physical properties did not differ from American pennyroyal oil either. Its constants were  $d_{16^\circ} 0,927$ ;  $n_D + 35^\circ$ ; content of pulegone 75 % (boiling point  $212$  to  $220^\circ$ ); soluble in 2 vol. 70 per cent. alcohol.

**Fennel Oil.** During this season we have again distilled here large parcels of foreign fennel, and we only carry stocks of our own distillate of exceptional quality, which owing to a very high anethol-content already solidifies at  $+6^\circ$ . By abstracting a portion of the anethol the oil can be cheapened, and for this reason the above solidifying point should be insisted upon in placing orders. We recently examined an oil which only solidified at  $+1,7^\circ$ , and from which consequently the bulk of the anethol had been abstracted.

The fennel grown on fields at Lützen, only a few miles from our own establishment, unfortunately cannot compete with fennel grown abroad, the less so, as the new Tariff reasonably allows freedom of duty to foreign seed for distillation.

Reports received from Salonica state that the fennel harvest in Macedonia in 1904 has given a yield of only 200000 kilos, which in view of the harvest of 7000000 kilos of the year 1903 seems hardly credible.

With the view of increasing the knowledge of fennel oil, we submitted, when distilling a large quantity Galician fennel, the first fractions of this oil to a closer examination. The terpenes detected up to the present in the low boiling portions of common fennel oil, were pinene and dipentene<sup>2</sup>). Tardy<sup>3</sup>) claimed to have discovered also phellandrene and cymene in an oil obtained from French bitter cultivated fennel, but he failed to give the necessary proofs of this. By our renewed examination we have detected camphene as a new constituent of fennel oil, and have shown that the oil contains  $\alpha$ -phellandrene. Cymene, however, could not be detected.

<sup>1</sup>) Pharm. Journ. **75** (1905), 861; Chemist and Druggist **67** (1905), 970.

<sup>2</sup>) Report April **1890**, 20.

<sup>3</sup>) Bull. Soc. Chim. III. **17** (1897), 660.

From 1152 kilos of Galician fennel oil distilled by ourselves, two fractions of the first runnings were obtained, each 12 kilos, which possessed the following properties:

Fraction I: reddish-yellow oil with a disagreeable basic odour, which on prolonged standing acquires an intense dark-red to black colour, and which has the following constants: —  $d_{15^{\circ}} 0,8604$ ;  $n_D +42^{\circ} 23'$ ;  $n_{D19^{\circ}} 1,46793$ ; boiling point  $158$  to  $181^{\circ}$  (759 mm. pressure). The bulk boils between  $159$  and  $161^{\circ}$ .

This fraction contains traces of basic constituents. When extracting the oil with dilute sulphuric acid and subsequently treating the aqueous acid solution with an excess of soda, there was obtained in extremely small quantity a base in the form of a faintly yellow coloured oil, which had a very unpleasant pyridine-like odour which gave rise to severe headache. It showed a feeble pyrrol-reaction and its hydrochloric solution gave with platinum chloride a platinum double salt which dissolved with difficulty in water, but the quantity of which was not sufficient for more detailed examination. This fraction of the first runnings of fennel oil further contained small quantities of aldehydes, for it imparted an intensely red colour to fuchsin sulphurous acid. But no unsoluble bisulphite compounds could be obtained by extraction with bisulphite liquor, and the oil only acquired a faint cherry-red colour after prolonged contact with the bisulphite liquor.

Fraction II of the first runnings of the fennel oil was a water white almost colourless liquid, which had neither a basic odour, nor gave an aldehyde reaction. In addition to a pronounced fenchone odour, it possessed an intensely bitter taste, and gave a strong phellandrene reaction. The constants of this fraction were:  $d_{15^{\circ}} 0,8879$ ,  $n_D +42^{\circ} 10'$ ,  $n_{D18,6^{\circ}} 1,47078$ , boiling point  $172$  to  $193^{\circ}$  (761 mm. pressure). The bulk passed over between  $180$  and  $185^{\circ}$ .

The two fractions of the first runnings were submitted to systematic, frequently repeated fractional distillation, in order to separate them further.

Pinene and camphene. For the detection of these terpenes served a fraction with the following properties: — colourless oil of the boiling point  $155,5$  to  $157,5^{\circ}$  (760 mm. pressure [distilled over sodium]);  $d_{15^{\circ}} 0,8610$ ;  $n_D +43^{\circ} 23'$ ;  $n_{D24,2^{\circ}} 1,45381$ . By the action of amyl nitrite and hydrochloric acid on the glacial acetic acid solution of this oil, pinene nitrosochloride of the melting point  $102^{\circ}$  was obtained, though only in a very small yield. The corresponding pinene nitrobenzylamine base produced from it crystallised from alcohol in colourless needles of the melting point  $122^{\circ}$ .<sup>1)</sup>

<sup>1)</sup> Comp. Report April 1890, 20.

When hydrating the same fraction by means of glacial acetic acid, a yellowish oil was formed which had the odour of isobornyl acetate, and passed over at 12 mm. pressure between 62 and 108° (the bulk at 65°). On saponifying the oil portions passing over above 95° with alcoholic potash, and treating the saponification product with water vapour, a colourless crystalline mass was obtained, which possessed the odour of isoborneol, and which after being recrystallised 4 to 5 times from petroleum ether, melted at 208 to 208,5°. The melting point of the isoborneol could not be raised further.

**Phellandrene.** Phellandrene was detected in a fraction of the following constants: —  $d_{15,5^{\circ}} 0,8733$ ,  $\alpha_D + 34^{\circ} 34'$ ,  $n_{D22,9^{\circ}} 1,47186$ , boiling point 49,2 to 55° (7 mm. pressure).

The crude nitrite of the phellandrene obtained in a rather low yield, was freed from the coarsest impurities by trituration with a cold mixture of methyl alcohol and ether, and crystallised from acetic ester. Frequent repetition of the crystallisation led to the  $\alpha$ -nitrite of  $\alpha$ -phellandrene, which was obtained in an approximately pure state in fine colourless needles of the melting point 114° (slowly heated) or 119° (rapidly heated). The specific rotation of this nitrite in chloroform solution was ascertained as  $[\alpha]_D - 133,4^{\circ}$ .

From the mother liquors of the crystallisation of the  $\alpha$ -nitrite there was obtained, by precipitating with 60 per cent. alcohol and dissolving in acetic ester, after repeating this operation several times, the  $\beta$ -nitrite of  $\alpha$ -phellandrene of the melting point 103 to 104°, in small needles, grouped in the form of stars, and in a not very pure condition. But it was at any rate possible to determine that the character of the specific rotation of this nitrite (in chloroform solution) was positive (found  $[\alpha]_D + 16,3^{\circ}$ ).

**Dipentene.** Dipentene<sup>1)</sup> was detected in fennel oil by brominating a fraction with the following properties: —  $d_{15^{\circ}} 0,8607$ ,  $\alpha_D + 37^{\circ} 25'$ , boiling point 63 to 67° (16 mm. pressure), boiling point 177,5 to 180,5° at 748,5 mm. pressure.

The dipentene tetrabromide melted after recrystallisation from methyl alcohol and subsequently from acetic ester at 124 to 125°.

**Absence of cymene.** For the test for cymene, which, according to Tardy<sup>2)</sup> is present in French fennel oil, we employed a fraction whose constants were as follows: — boiling point 176,2 to 180,5° (762 mm. pressure),  $\alpha_D + 23^{\circ} 56'$ ,  $n_{D23^{\circ}} 1,47422$ .

First of all this fraction was oxidised with cold 1 per cent. permanganate solution. In order to remove from this fraction any fenchone which may at the same time be present, and which cannot

<sup>1)</sup> Comp. Report April 1890, 20.

<sup>2)</sup> Bull. Soc. Chim. III. 17 (1897), 690.

be oxidised out in this manner, it was converted into the oxime of the melting point  $161^{\circ}$ , when the hydrocarbons were separated from the fenchone oxime by steam distillation. The yellowish oil then passing over was next further oxidised in the cold with 1 per cent. permanganate solution, during which operation its optical dextrorotation decreased gradually. Finally, there remained only 2,5 grams oil out of the 76 grams, with an angle of rotation  $\alpha_D$  of  $+12^{\circ}10'$ . These last oil portions were heated on a water bath with a solution of 5,04 grams potassium permanganate in 140 cc. water. But the oxidation yielded neither the p-oxyisopropyl benzoic acid characteristic of p-cymene, nor terephthalic acid. Only a very small quantity of a brown-yellow oil which could not be further identified was obtained in this reaction. Consequently p-cymene was not present in the fennel oil examined.

**Oil of Fool's parsley.** F. B. Power and F. Tutin<sup>1)</sup> have made a chemical examination of the herb of fool's parsley, *Aethusa cynapium* L., so much feared on account of its highly poisonous character. The herb gathered in July and August was extracted with alcohol in an air-dry condition, and the resulting extract distilled out with water vapour. The essential oil thereby obtained (0,015% of the weight of the fresh herb) was at first colourless, but soon acquired a dark-brown colour, and had an unpleasant odour. In the distillation water formic acid could be detected. The distillation residue (0,8% of the weight of the fresh herb) dissolved partly in petroleum ether. After saponifying the dissolved portion, there could be isolated from it pentatriacontane  $C_{35}H_{72}$  (melting point  $74^{\circ}$ ) and an alcohol (melting point  $140$  to  $141^{\circ}$ ;  $[\alpha]_D -35,7^{\circ}$ ), isomeric with phytosterol  $C_{26}H_{44}O$ , or a lower homologue. The saponification liquor contained formic acid and butyric acid. The portion insoluble in petroleum ether, when melted with potash, yielded formic, butyric, and proto-catechuic acids.

From the water which had remained behind in the retort after the distillation, there were isolated: d-mannite, melting point  $165$  to  $166^{\circ}$ , glucose, an amorphous dye, and a very small quantity of an alkaloid having an odour like conine. This base behaved in its chemical, physical and physiological reactions as coniine, and for this reason the toxic effect of the plant must probably be attributed to the presence of coniine in it.

**Geranium Oils.** During the last few years, the production has increased to such an extent in Algeria, that it has only been possible to force the demand by constant reductions in the prices. In

<sup>1)</sup> Journ. Soc. Chem. Ind. **24** (1905), 938.

order to prevent a further decline in the value of this article, a moderate restriction in the production might be advisable until such time as a suitable adjustment between supply and demand has been reached.

But it would probably be difficult, if not impossible to bring the Algerian producers all under one flag.

Energetic steps have been taken in Réunion. No. 1580 of *La Patrie Créole*, of 17<sup>th</sup> December 1905, contains the official news of the formation of a Syndicate for geranium oil, the legal formalities having been gone through on the 14<sup>th</sup> December, at the Mairie of St. Pierre. The Syndicate has been formed for a period of 5 years. At the meeting of 2<sup>nd</sup> December, the producers have for the protection of their interests established this Syndicate, to which at that time ten of the most important manufacturers belonged. According to more recent information, the number of producers belonging to the Syndicate on the 29<sup>th</sup> December had already increased to 104, and were said to represent nine tenths of the whole production of geranium oil. The depot for storing the product is also established at St. Pierre. The officials have already been appointed. But a result may possibly not be expected until the enormous stocks which have accumulated at Marseilles and elsewhere in the hands of speculators, have to some extent been cleared.

The selling prices have up to the present not yet undergone any appreciable change, and there does not appear to be any intention of engineering a rise, but on the contrary of raising the value gradually, by reducing the output to 30000 kilos per annum, until a figure is reached at which the industry can continue to exist.

The question now is, whether the Syndicate will succeed in keeping control over the entire export, and whether harmony can be maintained among the participants.

The most striking comment on the steps described above forms the following table of statistics: —

In 1901 there were exported 13953 kilos; the price was 43 francs								
"	1902	"	"	"	17193	"	"	36 "
"	1903	"	"	"	25323	"	"	29 "
"	1904	"	"	"	27660	"	"	27 "
"	1905	"	"	"	38334	"	"	24 "

In our opinion the World's annual consumption is overestimated at 30000 kilos, and it has been left out of account that at the same or similar prices, the much finer Algerian distillate may generally be preferred.

The so-called Indian geranium or palmarosa oil was at the beginning of the season in October placed on the market in large

quantities, and the extremely low price led to very important transactions. Larger orders at limited prices failed through opposition of the producers, to whom the low value is no longer remunerative. For this reason a decided advance had to be paid later on, and at the present moment advantageous purchases are quite impossible. The average price of our purchases forced us to raise our quotations.

An idea of the importance of this article may be gathered from the fact that the Export of geranium oil from Bombay, from 1<sup>st</sup> July 1904 to 30<sup>th</sup> June 1905, amounted to 162 990 lbs. of a value in round figures of £ 30000.

Of this quantity, quite one half consists of inferior qualities.

Exceptionally rare is this season the so-called gingergrass oil, and it remains questionable whether this oil can be offered in sufficient quantities.

A geranium oil produced in Sicily has been examined by Umney and Bennett<sup>1)</sup>. This product, which had a quite exceptionally pleasant odour, was obtained in a yield of 0,07 % from plants grown on a dry soil. The optical rotation of the 80 % first distilling over was 11°:  $d_{15}^{\circ}$  0,894; ester-content (geranyl tiglinat) 35,6 %; total geraniol 71,9 %; soluble in 2 vol. 80 per cent. alcohol; insoluble in 70 per cent. alcohol. The ester-content is therefore higher than in French or Algerian oils, but approaches very closely to the highest observed in Réunion geranium oil. In view of the small yield in which it was obtained in the distillation, it is doubtful whether the Sicilian oil will ever appear as a serious competitor against the oils met with in commerce.

**Hyssop Oil.** Owing to lack of distillation-material, we have temporarily been compelled to introduce the French distillate, which is inferior to the oil distilled from leaves and blossoms of the home-grown herb. But for the coming summer we have made the necessary arrangements to grow the material ourselves in sufficient quantities, so that we hope in the autumn to be able to offer again our own distillate.

**Oil of Juniper berries.** The high prices of the berries have now also affected the value of the common Hungarian distillate, of which only the absolutely necessary quantities can be obtained with great difficulty. This situation will continue until the coming winter,

**Lavender Oil.** Contrary to expectation, the distillers and principal merchants have succeeded in keeping up the high prices, and there does not appear to be a decided change in sight before the

<sup>1)</sup> Pharm. Journ. 75 (1905), 860; Chemist and Druggist 67 (1905), 970.

new harvest. At the same time, the interested French parties should not aim too high, as lavender oil can be replaced by bergamot oil, whose content of linalyl acetate equals that of a fine quality lavender oil, and as consumers may strike lavender oil out of many compositions owing to its high price. It may safely be assumed that next season the demand will be considerably less, and that the public will object to pay such high prices as last year.

We also are firmly resolved to act in such manner in the future, and nothing whatever will deter us from doing all we can to bring about again a sensible state of affairs.

As regards our controversy with the firm of Lautier Fils at Grasse, concerning the ester-content of the lavender oil distilled by us at Barrême, we maintain emphatically our assertion that we have obtained in the course of manufacture large quantities of lavender oils of up to 52<sup>0</sup>/<sub>0</sub> natural ester-content. However, we are pleased to acknowledge that Mr. Lautier has loyally declared his willingness to give us satisfaction if we convince him of his error. This is to take place in the course of next season by expert evidence.

With regard to the ester-question, we have discussed this matter in such detail in our Report of October 1897, pages 32 to 36, and have especially done justice to the odour-test, that it would serve no useful purpose to enter once more so fully into this point in dispute. This only we would state here, that the subsequent observations, made from 1897 to the present day, have only confirmed the correctness of the position taken up by us in this question.

In a book on Pharmacy in Burgundy prior to 1803 by A. Baudot<sup>1)</sup>, which deserves to be widely read, we find *inter alia* some details on the cultivation of lavender carried on at the Court of Burgundy in the 14<sup>th</sup> century, which we desire to quote here briefly on account of their particular interest.

In the year 1371 the then Duchess of Burgundy, who was particularly fond of lavender perfume, had a few expensive lavender stalks planted in the garden of the Castle of Rouvres and attempted at the same time the cultivation of lavender by sowing out seed. These efforts were continued with great perseverance and finally led to the desired result, so that later on it was possible to speak of a flourishing cultivation of lavender in the gardens of Rouvres. Hyssop, sage, violets, roses, and other aromatic plants were grown there with equally good results. Baudot believes that in such experimental gardens the first beginnings of our present-day botanical gardens may possibly be seen.

<sup>1)</sup> A. Baudot, *Études historiques sur la pharmacie en Bourgogne avant 1803* Paris 1905.

**Oil of Laurel leaves.** Of the constituents of oil of laurel leaves, Wallach<sup>1)</sup> detected in 1889 pinene and cineol. Ten years later we<sup>2)</sup> found that eugenol is also present in this oil, whilst H. Thoms and Molle<sup>3)</sup> demonstrated in 1904 that the oil also contains geraniol and a small quantity of free acids (acetic, butyric, valeric acids) and also esters of acetic, valeric and caproic(?) acids. They further obtained traces of a still unknown acid of the melting point 146 to 147°. On fractional distillation of 500 gr. oil of laurel leaves of our own make, we have now succeeded in detecting two further constituents, viz., linalool and eugenol methyl ether.

The oil examined had the following constants: —  $d_{15}^{\circ}$  0,930;  $a_D$  — 15° 26'. A fraction of the oil boiling at 67 to 85° (4 mm. pressure) had a distinct linalool odour. At ordinary pressure the boiling point lay between 195 to 204°.

In order to produce the linalool in the pure state, 21 gr. of the fraction were converted with sodium into the alcoholate, and the latter in ethereal solution decomposed with phthalic acid anhydride. After the impurities had been removed by dissolving the acid ester formed in soda, and extracting this solution with ether, there remained behind a solution of sodium linalylphthalate, which on being boiled with caustic potash separated off linalool. The pure linalool thus obtained and distilled *in vacuo*, had the following properties: boiling point 197 to 200° (762 mm. pressure);  $d_{15}^{\circ}$  0,8715;  $a_D$  — 11° 5';  $n_{D20}^{\circ}$  1,46387. The phenyl urethane melted at 65°. On oxidation with chromic acid citral was formed.

A fraction of the oil of laurel leaves boiling at 240 to 250° was characterised by the odour of methyl eugenol. Although this compound could not be obtained in the pure state, veratric acid was obtained on oxidation of this fraction with potassium permanganate, which confirms the presence of eugenol methyl ether. The acid recrystallised from alcohol and water melted at 178°. Its silver salt gave the following values on examination: —

I. 0,2512 gr. of the substance yielded 0,0945 gr. Ag.

I. 0,1380 " " " " " 0,0515 " Ag.

Found

Calculated

$C_6H_3(OCH_3)_2COO Ag.$

Ag 37,62, 37,33 %

Ag 37,37 %.

**Lemongrass Oil<sup>4)</sup>.** It would appear that Java will in the immediate future make competition to the Cochin distillate. Samples

<sup>1)</sup> Liebigs Annalen 252 (1889), 95.

<sup>2)</sup> Report April 1899, 31.

<sup>3)</sup> Arch. der Pharm. 242 (1904), 161.

<sup>4)</sup> Report October 1905, 44, read cocoa-nut oil instead of "cocoa-butter".

have already been approved many a long day since, and the first consignments may possibly make their appearance very soon. Since in the oil of *Backhousia citriodora* a new and very rich source of citral has also been discovered, which it may soon be possible to make use of in practice, the time for the exaggerated prices of lemongrass oil appears to be now past, and producers will do well to meet the trade with concessions.

A lemongrass oil originating from Ceylon examined by Sage<sup>1)</sup> which had been distilled at the Government Experimental Station at Peradeniya, had the following properties: —  $d_{15,5^{\circ}}$  0.899,  $n_D^{20}$  — 0,2°, citral-content 66,5%. In alcohol the oil dissolves badly; it only forms a clear solution with 1 vol. absolute alcohol, which, however, becomes cloudy when more solvent is added.

The oil shares this deficient solubility with the West Indian and African distillates which have frequently been referred to in these Reports<sup>2)</sup>. Both on account of the inferior solubility, and of the low citral-content, the oil must be characterised, in spite of the opposite view held by Mr. Sage, as an inferior product which cannot compete with a good East Indian commercial oil.

**Linaloe Oil.** The business which at one time was very much split up, has gradually passed into the hands of a few Mexican firms, who no doubt make a handsome profit out of it, for in the year 1895 we still distilled here a few thousand kilos of oil from imported wood at a cost-price which quite enabled us to compete. In the meantime the cheap sources of wood near the coast have become exhausted, and it was practically impossible to fetch the wood from a greater distance, owing to the heavy cost of transport.

The value of good oil has remained practically unchanged during the last six months.

The Cayenne distillate has a finer odour than the Mexican, and is preferred for certain products.

**Mustard Oil.** The prices of Indian mustard-seed have come out cheaper, so that we have again been able to undertake the regular working up of this kind of seed. Mustard oil remains an article of confidence in the fullest sense of the word. Our present selling price just covers the expenses. If a competition arises which offers pure oil from seed at still lower prices, and also supplies it pure, we shall have to give in!

<sup>1)</sup> Chemist and Druggist 68 (1906), 355.

<sup>2)</sup> Comp. Reports October 1902, 50; April 1903, 23, 49; October 1903, 46; October 1904, 53; April 1905, 85.

Our sale of artificial oil has increased to a considerable extent. In that line we can meet all competition.

In one of our last Reports<sup>1)</sup> we referred to a work on the quantitative estimation of mustard oil, by R. Firbas, in which it was *inter alia* pointed out, that if the method of estimation indicated in the German Pharmacopœia is exactly followed, the results obtained are too low, as the decomposition of the thiosinamine silver compound in the cold is not completely finished in 24 hours. By heating it, the values are raised in proportion to the period of the heating. Firbas obtained the highest results when heating in a pressure flask up to about 100°, but he leaves it an open question whether in this case the contaminations of the mustard oil, which are sparingly soluble, are not included in the estimation. We received the original work<sup>2)</sup> only at a late date, and now return to this subject, in order to reproduce a table in which Firbas has summarised the results obtained by him, and which will no doubt prove interesting to a larger circle of readers: —

	According to the German Pharmacopœia IV	According to the German Pharmacopœia IV after prolonged standing	According to the Commentary to the German Pharmacopœia IV by Fischer and Hartwich	According to the Commentary after 24 hours, heating	According to the Commentary when heating to 100°	According to K. Dietrich's method (Analyt. determination of weight of the silver sulphide)
Natural oil I . . . .	84,0	84,2	95,6	96,0	96,8	98,9
do. I . . . .	83,6	83,9	94,2	—	—	—
do. II . . . .	81,4	82,1	94,7	94,9	96,1	97,4
do. III . . . .	80,2	80,2	89,7	91,6	91,8	—
do. IV . . . .	84,7	—	91,2	92,4	—	95,3
Artificial oil I . . .	76,2	—	89,4	91,4	91,6	92,6
do. II . . . .	84,9	85,4	96,8	97,3	97,3	—

We have in recent times repeatedly had to make estimations of mustard oil of our own distillates, and have found Firbas' observations fully confirmed. The mustard oil determinations carried out exactly in accordance with the instructions of the German Pharmacopœia without heating, give in every case results which were about 8% too low, and according to these no mustard oil would satisfy the requirements of the Pharmacopœia. For this reason it is at the very least necessary to follow the directions given in Fischer-Hartwich's Commentary to the Pharmacopœia, and heat the flask for a

<sup>1)</sup> Report April 1904, 63.

<sup>2)</sup> Zeitschr. d. allgem. österr. Apoth. Ver. 58 (1904) 222.

short time after it has been left standing for 24 hours. As already mentioned above, the period during which the flask is heated, as well as the actual temperature, are here of importance, and definite information on this point is therefore required, if comparable results are to be obtained. The method followed by ourselves agrees with the one recommended by B. Fischer and C. Hartwich in the Commentary to the Pharmacopœia: About 5 gm. of a solution of 1 gm. mustard oil in 49 gm. alcohol are mixed in a measuring flask of 100 cc. capacity with 50 cc. deci-normal solution of silver nitrate and 10 cc. ammonia liquid ( $d_{15^{\circ}} 0.960$ ); the flask is then closed, and with frequent agitation left standing for 24 hours with the light excluded.

The flask is then placed for  $\frac{1}{2}$  hour<sup>1)</sup> in water at  $80^{\circ}$ , during which time it is again repeatedly shaken, next cooled down to the temperature of the room, filled up with water to the mark, shaken up, and filtered. 50 cc. of the filtrate are titrated with  $\frac{1}{10}$ <sup>th</sup> normal solution of ammonium sulphocyanide, after adding 6 cc. nitric acid ( $d_{15^{\circ}} 1.153$ ) and a small quantity of solution of iron alum, until a change of colour from white to red takes place. In order to ascertain the whole quantity of silver solution which has entered into reaction, the number of cc. of ammonium sulphocyanide solution used up is doubled, and the product subtracted from 50. The percentage of allyl isothiocyanate in the mustard oil is obtained by means of the following formula: —

$$\% \text{CSNC}_3\text{H}_5 = \frac{a \cdot 24.7875}{b}$$

a = number of cc. of deci-normal solution of silver nitrate used up.  
b = spirit of mustard used up in grammes.

Mustard oil determinations carried out by us in the manner described, showed in the case of natural oil a content of about 94% allyl isothiocyanate, whilst in artificial oil about 98% were determined.

**Myrrh Oil.** As a continuation of his work on secretions, A. Tschirch<sup>2)</sup> gives some information on Herabol myrrh which he, jointly with W. Bergmann, has submitted to a more detailed examination. Although the Pharmacopœias pronounce themselves very distinctly on the mother-plant of official myrrh, Tschirch considers it premature to indicate any definite species; the only thing certain is, that a *Commiphora* species of North East Africa yields the drug. From the material under examination, the so-called *myrrha electa* of commerce, the authors obtained 6 to 7% of an essential oil, by

<sup>1)</sup> According to Firbas the conversion is not entirely completed within the time, but we purposely do not heat for too long a period in order to avoid as much as possible the co-determination of the contaminations which are more difficult to decompose.

<sup>2)</sup> Arch. der Pharm. **243** (1905), 641.

exhausting the ethereal solution of the myrrh with one per cent. potash liquor, then washing with water, and after driving off the ether, distilling the residue with water vapour. The oil obtained had a honey-yellow colour, and was fairly viscid; it had a specific gravity of 1,046 and resinified readily. When exposed to the light, the oil quickly acquired a reddish-brown colour. From the residue of the steam distillation, the authors were able, after adding 1<sup>0</sup>/<sub>00</sub> potassium hydrate to obtain by further distillation another 1<sup>1</sup>/<sub>2</sub><sup>0</sup>/<sub>0</sub> of a secondary essential oil. Tschirch and Bergmann further determined the following constituents of myrrh: —  $\alpha$ - and  $\beta$ -herabo-myrrholol,  $\alpha$ - and  $\beta$ -herabo-myrrhol, heraboresene, a gum and an enzyme.

**Myrtle Oil.** In the higher boiling portions of myrtle oil, H. v. Soden and Fr. Elze<sup>1)</sup> have discovered a new alcohol of the formula  $C_{10}H_{18}O$ , which they have designated myrtenol. Myrtenol, which occurs in the oil chiefly as acetic ester, was obtained by saponification of the ester fraction with alcoholic potash liquor. By conversion into the phthalic ester acid melting at 116°, the myrtenol could be separated from admixtures of other alcohols, for example geraniol. From the phthalic ester acid, the new alcohol is obtained as a viscid, colourless oil with the odour of myrtle. Boiling point 220 to 221° (751 mm. pressure); 79,5 to 80° (3,5 mm. pressure);  $d_{15}^0$  0,985;  $\alpha_D + 49^0 25'$ . Myrtenol can be acetylated quantitatively, and appears to be a primary cyclic terpene alcohol.

**Nepeta Oil.** A Sicilian nepeta oil, whose more exact origin could not be determined, has been examined by Umney and Bennett<sup>2)</sup>. Its constants were  $d_{16}^0$  0,927,  $\alpha_D + 12^0$ ; total alcohol content (menthol) 22,2<sup>0</sup>/<sub>0</sub>; ester content (menthyl acetate) 3,3<sup>0</sup>/<sub>0</sub>; soluble in 2 vol. 70 per cent. alcohol. Small quantities of a ketone, possibly menthone or pulegone, appeared to be contained in the oil.

**Neroli Oil.** The most recent information on the prospects of the harvest of orange-blossoms in the South of France, which commences next month, are very unfavourable. The frost of the last days of March is said to have destroyed half the blossoms. The high prices may consequently continue in force. It is an undeniable fact that these high prices have greatly interfered with the sale of the natural oil, and have in many cases led to the introduction of the artificial oil which is now produced in such a high degree of perfection. Although under normal conditions of value the two oils may go alongside each other, when the difference is so enormous as last year, it becomes a matter of necessity for many to make use of the advantages which the artificial product offers.

<sup>1)</sup> Chem. Ztg. **29** (1905), 1031.

<sup>2)</sup> Pharm. Journal **75** (1905), 861; Chemist and Druggist **67** (1905), 970.

The matters in dispute between the manufacturers and the growers in the South of France are still unsettled. The latter, to the number of about 1400, have jointly established works at Vallauris, said to be capable of distilling 1400000 to 1500000 kilos blossoms. Operations will be commenced there if the manufacturers refuse to pay a price for the blossoms which enables the growers to earn a living, and to continue the cultivation.

**Orris Oil.** On the present position of the orris-root market we receive from our friends in Florence the following information: —

According to our previous report the quantity at disposal at the beginning of September 1905 amounted to . . . . .	about 560 tons
added to this, the result of the last harvest . . . . .	„ 650 „
makes a total of about 1210 tons.	

If we deduct the shipments from the beginning of September 1905 to the end of February 1906 . . . . .	„ 550 „
there remains at disposal, at the end of February 1906 . .	about 660 tons.

The export during the present season will apparently be a very large one, as from the beginning of September 1905 to the end of February 1906, that is to say in only 6 months' time, already 550 tons have been shipped, as against a total export of only 500 tons during the preceding 12 months, 1<sup>st</sup> September 1904 to 31<sup>st</sup> August 1905.

As compared with the last crop (1905) of 650 tons, we had in 1904 a crop of 670 tons, in 1903 of 750 tons, and in 1902 of 1000 tons.

The quality of the last crop has with few exceptions again turned out inferior, as too little care is bestowed upon the cultivation. The new plantings have again been reduced by about 10%. The demand has, since the beginning of September, constantly been good; France especially has bought a good deal, and is still in the market. The consequence is a continued advance in the prices. At the commencement of the harvest it was possible to buy assorted roots at 36/37 marks cif. Hamburg; now they are quoted 48/50 marks. Of seconds, which were last paid 45 marks cif. Hamburg, hardly anything can at present be obtained. With regard to the prospects of the next harvest we believe that, in view of the smaller quantities planted out in recent years, not more than 500 tons may be reckoned upon. The further movement of the prices during the present season will naturally depend in the first place upon the demand; if this should continue as at present, not much would remain of the existing stocks by the time of the new harvest, and this might easily have an upward effect upon the prices of the latter. The big demand from France appears to point to the fact that the old stocks there have been used up, which is all the more probable, as France was buying so little in the previous year. This would also explain the small export of but 500 tons during the 12 months from 1<sup>st</sup> September 1904 to 31<sup>st</sup> August 1905, whilst the world's annual consumption is estimated at about 900 tons.

Veronese orris has also advanced considerably. The so-called "mercantile" quality, which last autumn could be bought at 22 marks, now fetches 33 marks cif. Hamburg, with very small stocks. In the other Veronese qualities, No. 1 and No. 2, a great scarcity also exists, as the last crop, as is well known, was a very small one.

Taking all together, the probability is that high prices of orris-root must be looked for in future.

After such an important advance in the prices, amounting now to about 50 0/0, it was impossible to retain the quotations of orris oil which had been based upon the lowest purchase prices of the previous year. We have, however, raised our quotations for the present so little, that the advance represents a scarcely noticeable charge to the consumer, and in view of the situation we can only advise our friends to lay in an abundant supply at the present prices.

**Patchouli Oil.** After the prices had been forced down to the extreme limit, the downward movement has come to a stop. Good, healthy patchouli-leaves from Penang reached their lowest level in December last year with 25/- per cwt., but they advanced shortly afterwards to 28/- and cannot now be bought below 30/-. The low prices of oil have been largely taken advantage of; they bring profit to the perfumer in a double sense, as it is a well-known fact that the quality improves by prolonged keeping.

In the Botanical Garden of Buitenzorg there are three varieties of patchouli: I. *Patchouli fleurissant* (*Pogostemon Heyneanus* Bth.?), II. *P. de Singapour* (*Pog. tomentosus* Hassk.?), III. *P. de Java* (a variety of *Pog. tomentosus* Hassk.?), whose essential oils, according to A. W. K. de Jong<sup>1)</sup> possess the following properties:

	I.	II.	III.
d <sub>25°</sub>	0,922	0,949	0,929
[α] <sub>D25°</sub>	— 16° 10'	— 51° 24'	42° 48' 2)
Soluble in:	10 vol. 90 per cent. alcohol	6 vol. 90 per cent. alcohol	0,75 vol. 90 per cent. alcohol
Distillation at			
740 mm. up to 250°:	130 to 250° = 17 0/0	230 to 250° = 2 0/0	145 to 250° = 10 0/0
250 to 270°	50 0/0	60 0/0	70 0/0
270 to 280°	16 0/0	20 0/0	8 0/0
280 to 300°	10 0/0	10 0/0	6 0/0

The oils II and III contained Gladstone's azulene. The action of concentrated sulphuric acid left unchanged 17 0/0 of I, 22 0/0 of II, and 20 0/0 of III, from which was obtained by distillation a sesquiterpene (boiling point 260 to 263° at 740 mm. pressure) for which the author proposes the name dilemene. [α]<sub>D25°</sub>: II. — 1°, III. — 1,5°; d<sub>25°</sub>: II. 0,915, III. 0,897. This sesquiterpene de Jong considers possibly identical with the sesquiterpene (boiling point 273 to 274° at 760 mm pressure: [α]<sub>D</sub> + 0° 45'; d 0,930), discovered by von Soden and Rojahn<sup>3)</sup> in patchouli oil.

<sup>1)</sup> Recueil des trav. chim. des P.-B. **24** (2905), 309 to 312, Buitenzorg. Acc. to Chem. Centralbl. **1905**, II. 1180.

<sup>2)</sup> The sign denoting the direction of the rotation is not mentioned in the Report.

<sup>3)</sup> Berl. Berichte **37** (1904), 3354. Report April **1905**, 61.

According to a communication by P. Serre<sup>1</sup>) on the patchouli industry in Java and the Straits, the patchouli plants cultivated there also originate from *Pogostemon patchouli*; when fully developed they reach a height of 2 to 3 feet. The harvest of the leaves (which are sent to Europe in a well-dried state) commences as soon as the plants are 6" high; every six months the leaves are stripped again. The Malays put patchouli leaves in their mattresses and clothes to keep away insects. The yield of oil produced in the factories of those countries amounts to only a few per cent., owing to defective distilling apparatus; the yellow-green to dark-brown oil is very thick, and separates off crystals of patchouli alcohol. With the plants imported in Java, good results have been obtained up to an elevation of 1600 feet, but in Serre's opinion the oil obtained is of a lower quality than that produced in the Malacca Peninsula.

**Peppermint Oil, American.** The reports received from the principal districts of the peppermint oil production all agree, that the damage done to the fields by the winter-frosts turns out to be severe. The total absence of snow has allowed the frost to act direct on the plants, and to destroy a number of them, especially in Michigan. For this reason a certain falling off in the production must be expected next autumn, but against a too pessimistic interpretation of such communications should be warned, for experience shows that interested parties are apt to exaggerate, and in the course of the summer the traces of such damage very often dwindle down. But what should be specially taken into consideration, is that the quantity planted out has been considerably increased during the last two years, since the good prices obtained had again made the cultivation and distillation of peppermint a very remunerative occupation.

The present opportunity has naturally been taken advantage of in America to drive up the market-prices of crude oil, and the European markets have also followed the lead from the other side. The increase in the price from the beginning of January to the present moment amounts to fully 20%. Normal crude oil cannot be purchased to-day below 3,25 dollars.

Our New York branch, whose purchases come to about 30000 lbs. per annum, called our attention to the superior quality of the 1905 oil already on shipping the first parcels of the distillate of that year, and we have found this fully confirmed. In Japan it is hoped that America, in consequence of the present state of affairs, will appear as a heavy buyer of Japanese oil. There is nothing in this, if the latter is not used for mixing with the American oil, such as was the case some 3 or 4 years ago, at the time of the \$ 5,— price. In

<sup>1</sup>) Journ. d'agriculture tropicale 5 (1905), 369.

any case, it will be advisable to pay in future close attention to the common marketable qualities.

When fixing the prices of our two brands, we took into account the advantageous purchases made by us before the "frost"-situation, and we consider ourselves justified in advising a moderate cover at the present quotations. We will in future, as heretofore, do all we can to further the interests of the consumers of our brands, and will as energetically oppose any unwarranted or exaggerated upward movement, as we have successfully done in former years.

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On the 28<sup>th</sup> December 1905, the U. S. Department of Agriculture published a work by Alice Henkel, Assistant examiner of drug-plants, which gives interesting and partly new information on the history, cultivation, and utilisation of the peppermint-plant, and of which we reproduce below an abstract, from which the purely botanical details have been omitted: —

One of the most important oils produced in the United States is the one obtained from the peppermint-plant and varieties. The three kinds of mint which are cultivated in that country, are the so-called American mint (*Mentha piperita* L.), the black mint (*Mentha piperita vulgaris* Sale), and the white mint (*Mentha piperita officinalis* Sale); the two last-named are varieties of the first.

The peppermint or American mint is now grown in many parts of the Eastern States, and is found in the damp soil of New England States as far as Minnesota, and to the South as far as Florida and Tennessee. The black mint is harder and yields more than the other two kinds, and comes under consideration for practically all peppermint-farms. The white mint no doubt yields a very fine oil, but is little cultivated, owing to its sensitiveness and small yield.

Peppermint was first grown on a larger scale in 1816 in Wayne County, N. Y. Neighbouring counties also took up the cultivation, but Wayne County was and remains to this day the principal peppermint district in the State of New York.

The cultivation was then gradually extended to the Ashtabula, Geauga, and Cuyahoga County in Ohio, and also to Northern Indiana. Roots were introduced from Ohio into St. Joseph County, Michigan, and the first roots were planted in the Pigeon prairie in the year 1835. In the following years, the cultivation in the last-named State extended more and more, and since 35 years it has developed into the greatest peppermint producing section of the United States.

About 1844, an interesting "peppermint oil monopoly" was taken up by a New York firm, which apparently brought the cultivation in the State of Ohio to an end.

The first step consisted of this, that the firm sent a representative to Liverpool, to make inquiries about the consumption in England, which at that time is said to have amounted to 12000 lbs. per year. Another agent was sent to the West to ascertain the annual production, with the result that Wayne County N. Y. did not produce enough, Ohio too much, and the plantations in Michigan about the above-mentioned quantity of the English consumption. The agent of the firm now bound the producers of the States of New York and Ohio, under a high penalty, to plough up their peppermint fields, destroy the roots, and neither plant mint nor sell roots or oil for a period of five years. In consideration of this the producers received an allowance of 1,50 dollar per acre. The firm secured by contract the entire oil production of St. Joseph County, Mich., at the price of 2,50 dollars per lb. for a period of five years. The extension of the plantations and the sale of roots were also forbidden by contract. The producers carried out their engagements for three years, after which time the New York firm no longer laid stress upon the observance of the contracts, as it had meanwhile made a fortune out of the monopoly.

Since that period the area devoted to the cultivation of peppermint in Michigan has constantly extended, and Northern Indiana with the principal producing centres St. Joseph, Steuben, and La Grange County, also places continuously important quantities of oil on the market. In Ohio the cultivation has been given up, and in the State of New York the production has for years been cut down, until recently it has again acquired larger dimensions. Whilst in the year 1889 in Wayne County 3325 acres were planted with mint, the cultivation gradually declined until in 1899 it amounted to 300 acres, but it rose again to 933 acres in 1905.

The foregoing Report mentions finally that the good prices of oil of the last few years have induced many planters in the most diverse places to extend the cultivation of peppermint. This is not only the case in Michigan and Indiana, but also in the State of New York. For this reason a larger production of oil may be anticipated for the next few years, if favourable conditions prevail, and this is bound to have a depressing effect on the quotations.

The state of the market must therefore be kept under close observation, for the expenses of the cultivation amount to 12 to 14 dollars per acre, and those of the oil-distillation to 25 cents per lb. oil, so that the market-price of the oil may readily again fall below the cost of production.

**Peppermint Oil, Japanese.** The confidently expected drop in the prices has up to now been prevented by speculative enterprise. Japanese exporters are said to have sold large parcels of oil and

crystals for forward delivery at low prices, and to be compelled shortly to cover these. Knowing this, the Japanese are holding back offers, although the stocks in Japan must still be very heavy, and at the end of year were estimated at 150000 to 180000 lbs. The stocks in London and Hamburg are probably also fairly large, and moreover were bought dear, so that in both these places the tendency will be to keep the prices up.

The disposition in Japan is at this moment firm. The Japanese explain this in the following manner: — the cultivation of peppermint in the coming season will probably be greatly restricted, as the farmers do not find the present prices remunerative. The intention is, in case of need to warehouse the stocks and wait for better times. In this connection, however, the Japanese appear to forget that peppermint oil is not an article which lends itself to warehousing, as the quality suffers from age and from prolonged contact with the tin of the cases. To store the oil up for many years is therefore out of the question.

In our opinion the present value is low, and it does not appear advisable to speculate for still lower prices.

The total shipments from Japan of liquid oil and menthol during the year 1905, are as follows: —

	Peppermint Oil	Menthol
January	32 325 kin.	23 391 kin.
February	29 400 „	21 304 „
March	25 345 „	25 982 „
April	19 350 „	15 635 „
May	7 521 „	14 517 „
June	942 „	6 472 „
July	5 321 „	5 193 „
August	8 409 „	6 167 „
September	7 032 „	1 725 „
October	6 567 „	8 137 „
November	13 470 „	15 377 „
December	about 12 000 „	about 13 000 „
Total	167 684 kin	156 900 kin 167 684 „

Total oil and crystals  $324\,584 \text{ kin} \text{ à } 600 \text{ gm.}$   
 $= 194\,750 \text{ kilos.}$

According to the Financial and Economic Year book of Japan, published by the Imperial Ministry of Finance at Tokyo, the total value of the shipments of peppermint oil to the individual countries during the previous five years was as follows: —

	1900	1901	1902	1903	1904
	Yen	Yen	Yen	Yen	Yen
to British America . . . . .	—	—	—	2606	27450
„ France . . . . .	—	3436	7459	12593	60326
„ Germany . . . . .	16911	16942	50889	92351	95399
„ the United Kingdom . . . . .	—	13942	32175	57854	122738
„ Hong Kong . . . . .	28335	69572	59800	86691	163676
„ the United States . . . . .	—	—	12309	20682	74105
„ other countries . . . . .	5725	4546	2215	4839	15255
Total	50971	108238	164847	277616	558949

The Report of Roure-Bertrand fils<sup>1)</sup> of Grasse contains an interesting work by Marin Molliard on "*Menthe basiliquée*". Under this designation is understood a degeneration of the peppermint plant frequently observed in the South of France, which shows itself in a completely altered appearance as compared with the normal plant<sup>2)</sup>. The change consists of this, that the stalks and twigs which normally would run into inflorescences, never again form blossoms, but only leaves closely bunched together. The large leaves at the base of the altered twigs also show in their shape characteristic differences from the normal leaves of the peppermint; they are, namely, contrary to the latter, almost sessile, have a hand-shaped nervature, and a scarcely dentated edge. The stalk of the altered plant, of which the section is originally square, shows in the ramification a more and more circular section. These morphological and anatomical changes are caused, according to Molliard's researches, by a parasitism of acarides belonging to the group phytoptides and the family eriophyes. We would in this place only refer to the detailed description of the parasite to which Molliard has given the name "*Eriophyes menthae*". The acarides already attack the twigs of the peppermint plant at the moment when they are just breaking through the earth. The outer leaves undergo the least change, as they are soon left by the parasites, which endeavour to settle at the point of the newly forming leaf-buds. The younger leaves, however, which have to develop entirely in the presence of the parasites, suffer most from the destructive action of the acarides.

Up to the middle of July the parasites are found in large numbers on the twigs altered by them; they then disappear gradually. They hibernate apparently in the earth close to the stem or on its surface.

<sup>1)</sup> Reports of Roure-Bertrand fils, Grasse. October 1905, 3.

<sup>2)</sup> Comp. also Gildemeister and Hoffmann, "The Volatile Oils", p. 649.

in order to produce again the same malformation in the following year. Up to the present no practical remedy is known to protect the peppermint plant from the attack of the eriophyes.

In continuation of a previous communication<sup>1)</sup> on Sicilian peppermint oils, Umney and Bennett<sup>2)</sup> report on a third oil of the same origin, which had been distilled in July 1905. It agrees completely in its properties with the oil distilled in July 1904: —  $d_{15}^{\circ}$  0,906;  $\alpha_D$  —  $21^{\circ}$ ; total menthol 41,6%; ester (menthyl acetate) 6,0%; free menthol 36,9%; soluble in 3 volumes 70 per cent. alcohol.

**Petitgrain Oils.** Whilst the real petitgrain oil, the essential oil from the leaves and twig-ends of the bitter orange (*Citrus bigaradia* Risso) has already repeatedly been examined, the constituents of the essential oil obtained from the leaves and twigs of the sweet orange (*Citrus aurantium* Risso) are still unknown. An examination made by G. Litterer<sup>3)</sup> according to the usual methods, disclosed as principal constituents citral, geraniol, camphene and limonene. The constants of the oil were;  $d_{15}^{\circ}$  0,8603,  $\alpha_D$  +  $56^{\circ}46'$ ,  $n_{D20}^{\circ}$  1,472.

The citral, representing 4% of the oil, was isolated by shaking with sodium sulphite liquor. The semicarbazone melted at  $163^{\circ}$ , the citryl naphthocinchonic acid at  $197^{\circ}$ . The portion of the oil from which the citral had been removed contained 4,1% ester, calculated for  $C_{10}H_{17}O \cdot COCH_3$ . The acetylation showed a content of 19,7% alcohols of the formula  $C_{10}H_{18}O$ . Of these, 12,7% combined with phthalic acid (geraniol). After saponification of the portions separated from the citral, they were fractionated, and in the terpene fractions were detected, camphene by conversion into isoborneol, and limonene by its tetrabromide (melting point  $104^{\circ}$ ). In the higher-boiling fractions linalool was apparently also present, besides geraniol, but its presence could not be proved owing to the small quantity. Geraniol was isolated by means of the calcium chloride compound.

An oil<sup>4)</sup> produced by the same author<sup>5)</sup> from the leaves and twig-ends of the lemon tree (*Citrus limonum* Risso) had the specific gravity 0,8824 at  $15^{\circ}$ ;  $\alpha_D$  +  $21^{\circ}08'$ ;  $n_{D20}^{\circ}$  1,4725. From this oil 24% citral were isolated. The semicarbazone melted at  $162$  to  $164^{\circ}$ , the citryl naphthochinchonic acid at  $197^{\circ}$ .

<sup>1)</sup> Report October 1905, 57.

<sup>2)</sup> Pharmac. Journal 75 (1905), 860; Chemist and Druggist 67 (1905), 970.

<sup>3)</sup> Bull. Soc. Chim. III. 33 (1905), 1079.

<sup>4)</sup> An oil of this kind has repeatedly been described by us. Citral had also been detected by us already before. Comp. Report October 1896, 59; April 1902, 79; April 1905, 64.

<sup>5)</sup> Bull. Soc. Chim. III. 33 (1905), 1081.

Citronellal could not be detected. The oil from which the citral had been removed contained 10,5% ester, calculated for  $C_{10}H_{17}H \cdot COCH_3$ , and 11,2% free geraniol. After saponification, limonene was detected (by the tetrabromide) in the terpene fractions. Camphene could not be obtained with absolute certainty. In the higher-boiling fractions linalool is probably present. The presence of geraniol was proved by the boiling point, and the formation of citral.

In a Sicilian oil of lemon leaves (*Petitgrain citronnier*) Umney and Bennett<sup>1)</sup> ascertained the following physical constants:  $d_{15^\circ} 0,873$ ,  $\alpha_D +26^\circ$ ; ester content 9,4%; aldehyde content 29%; total content of alcohol 38,9%. The first 30% of the product passed over between 175 and 180°.

**Pimento Oil.** We offer only our own distillate, and have again been able to reduce its price.

**Pine-needle Oils.** There is a great scarcity of all kinds, as far as pure original distillates are concerned. Particularly scarce is the oil of *Pinus pumilio*, the so-called "Latschenkiefer", and an examination of the products met with in commerce under this name has led to the result that they are almost without exception substitutes. Further, this oil from the "Latschenkiefer" grown in the lowlands appears to be of a different character to that from the trees in the Tyrolese mountains. We hope that we shall succeed in clearing up this matter by comparing our own distillates, and this seems to us all the more necessary, as the oil of *Pinus pumilio* finds a constantly growing use as a medicament.

The production of the very popular oil from the Siberian pine-needle, *Abies Sibirica*, appears to have been neglected entirely owing to the internal troubles in Russia; at present it can only be obtained in small parcels, which is very annoying, as the oil has become thoroughly introduced.

The oil from the needles of *Abies alba* is also supplied in insufficient quantities, but as it is not officinal, it can in case of need better be dispensed with than the oil of *Pinus pumilio*.

It is much to be hoped that new sources of supply of good conifer-distillates will soon be opened up.

We have recently had occasion to distil ourselves oils of *Pinus pumilio* and of the needles of *Abies alba*, and we give below the properties of the distillates obtained by us. The distillation material had been obtained from Styria, and was worked up cut in very small pieces.

Oil from *Pinus pumilio*. The yield of crude oil (coloured yellow) was 0,41%. The oil begins to boil at 170° (746 mm.); at 203°,

<sup>1)</sup> Pharm. Journal **75** (1905), 861; Chemist and Druggist **67** (1905), 970.

67% had distilled over;  $d_{15^\circ}$  0,8685;  $\alpha_D$   $-11^\circ 3'$ ; acid number 1,4; ester number 16,8 = 5,9% bornyl acetate; soluble in about 5,5 or more vol. 90 per cent. alcohol.

Oil from the needles of *Abies alba*. Yield 0,56%;  $d_{15^\circ}$  0,8852;  $\alpha_D$   $-34^\circ 55'$ ; acid number 0,9; ester number 17,5 = 6,1% bornyl acetate; soluble in about 6,5 and more vol. 90 per cent. alcohol. The oil begins to boil at  $162^\circ$ ; up to  $185^\circ$ , 55% passed over.

An oil from the needles of *Abies alba*, distilled from the same material but cut up in coarse pieces, showed slight differences which are probably due to a somewhat smaller content of sesquiterpene as compared with the oil just described: —  $d_{15^\circ}$  0,8845;  $\alpha_D$   $-35^\circ 34'$ ; acid number 1,3; ester number 21,2 = 7,4% bornyl acetate; soluble in about 5,5 and more vol. 90 per cent. alcohol.

These oils from the needles of *Abies alba*, distilled by ourselves, have a higher specific gravity than the distillates originating from Switzerland and the Tyrol, in which it lies between 0,869 and 0,875. But in the distillates produced in Upper and Lower Austria we have always found higher specific gravities, up to 0,886, so that the origin should be taken into account when judging the oils.

Oil from *Pinus laricio*. Two distillates sent to us, said to be derived from the needles of *Pinus laricio* Poiret, behaved as follows:

- a.  $d_{15^\circ}$  0,8646;  $\alpha_D$   $+8^\circ 17'$ ; ester number 2,9 = 1,0% bornyl acetate; soluble in 8 to 9 and more vol. 90 per cent. alcohol.
- b.  $d_{15^\circ}$  0,8701;  $\alpha_D$   $+3^\circ 29'$ ; ester number 9,8 = 3,4% bornyl acetate; soluble in 8 vol. 90 per cent. alcohol.

Both oils were colourless, and had a pleasant balsamic odour.

Oil from *Pinus maritima*. E. Belloni<sup>1)</sup> reports on his examinations of the essential oil from the shoots of *Pinus maritima* Mill. On distilling the fresh shoots gathered in the South of France, the author obtained a yield of 0,681% and when using dried shoots of 0,517%, of a bright-green essential oil possessing an aromatic taste and characteristic pine needle odour. Belloni determined the following constants: —

A. Oil from fresh shoots:  $d_{15^\circ}$  0,8810,  $\alpha_D$   $-23^\circ 46'$ ,  $[\alpha]_{D15^\circ}$   $-26,518^\circ$ , acid number 0, ester number 7,9; saponification number 7,9, ester 2,77% (calculated for  $C_{10}H_{17}O \cdot CO \cdot CH_3$ ), combined alcohol 2,13%.

B. Oil from dried shoots:  $d_{15^\circ}$  0,8963,  $\alpha_D$   $-20^\circ 15'$ ,  $[\alpha]_{D15^\circ}$   $-22,355^\circ$ , acid number 5,43, ester number 8,27, saponification number 13,7, ester 2,92% (calculated for  $C_{10}H_{17}O \cdot CO \cdot CH_3$ ); free alcohol 11,9%; combined alcohol 2,28%, total alcohol 14,18%.

<sup>1)</sup> According to reprint kindly sent us. "Sull' essenza di gemme di *Pinus maritima* Mill." Milan 1905. Estr. dall' Annuario della Soc. Chim. di Milano 11 (1905). Comp. Chem. Centralbl. 1906, I. 360.

The oils are insoluble in 80 per cent. alcohol, soluble in 10 vol. 90 per cent. alcohol; they are miscible with 95 per cent. and stronger alcohol.

On fractional distillation in a Ladenburg flask, there passed over, of oil A: between 155 and 170°, 58% ( $\alpha_D - 27^\circ 50'$ ), between 170 and 190°, 20% ( $\alpha_D - 31^\circ 40'$ ), residue 20%. Of oil B there distilled between 155 and 170°, 42% ( $\alpha_D - 26^\circ 42'$ ), from 170 to 190°, 20% ( $\alpha_D - 29^\circ 34'$ ), residue 37%.

The oil of *Pinus maritima* contains no aldehydes; the free acid of the oil obtained from dried shoots consists chiefly of caprylic acid (about 1,396%). In the formation of ester, only lower fatty acids appear to take part, probably acetic acid, propionic acid, caprylic acid, and laurinic acid. The bulk of the oil, according to Belloni, consists of l-pinene, of which he determined the following constants:  $d_{15^\circ} 0,86186$ ,  $[\alpha]_{D15^\circ} - 29^\circ 30'$ , boiling point 155 to 157°. (Nitrosochloride melting point 103°, nitrolpiperidide melting point 118°.) Phellandrene and sylvestrene could not be detected in the fraction passing over from 170 to 190°, but the presence of limonene is probable, either in the optically active form, or inactive as dipentene. The alcohols of the oil could not be identified; although the odour pointed to the presence of borneol esters, it was not possible to isolate borneol.

When producing the pinene nitrolpiperidide, Belloni observed that, when the alcoholic solution of the nitrosochloride is heated for a prolonged time with piperidine on the water bath, there are formed in the place of pinene nitrolpiperidide, needle-shaped crystals of the nitrosopinene (melting point 131 to 132°). Piperidine acts therefore, with prolonged heating, the same as potassium hydrate or diethylamine, which convert nitrosochloride into nitrosopinene.

**Rose Oil.** The prices of the better-class brands of really pure quality have kept at the same level throughout the season, but ordinary market-qualities, of which the bulk of the sales consists, could be bought about 30% cheaper. The official export-figures of the last two years are as follows: —

Rose oil export from 1<sup>st</sup> January to 31<sup>st</sup> December.

	1905	1904
to Austria-Hungary . . . . .	23 kilos	23 kilos
„ the United Kingdom . . . . .	891 „	472 „
„ Germany . . . . .	714 „	853 „
„ Turkey . . . . .	230 „	578 „
„ France . . . . .	1529 „	1445 „
„ the United States, Russia, Italy, Belgium, etc. . . . .	1929 „	1023 „
Total	5316 kilos	4394 kilos

The stocks in hand of the various qualities are estimated at about 650 kilos.

With the exceptionally mild winter, the rose-fields have up to the present suffered no damage whatever, and at this moment the prospects of the new harvest are very favourable. It is to be hoped that they will not be affected by belated night-frosts. With regard to the yield, nothing certain can be said before the end of May.

During the examination of consignments of rose oil, W. H. Simmons<sup>1)</sup> observed in two cases the presence of ethyl alcohol. As in both cases only very small quantities of alcohol (0,65 and 1 0/100 respectively) were detected, Simmons attributes their presence more to an accident than to an intentional adulteration, but in the case of an expensive article like rose oil a small alcohol-content is also important, especially when it is a question of the purchase of large quantities. Simmons does not believe that processes of fermentation play here a part, such as we have once before observed with our own distillates<sup>2)</sup>, as the samples belonging to the consignments did not contain alcohol.

Simmons avails himself of the opportunity to point out that the index of refraction may occasionally be of some value for judging rose oil; he mentions 1,4600 as the lowest permissible value for 20°. We have observed in good oils at 25° refractive indices between 1,452 and 1,464<sup>3)</sup>.

**Rosemary Oil.** Both the Dalmatian and the French oils suffered from a slow demand. The distillers of the former may possibly be compelled to make concessions in the price, in order to dispose of their product. The manufacturers in the South of France already show themselves more accommodating.

**Sandalwood Oil.** The parcels of sandalwood purchased by us at the last auctions, have now all arrived.

The official statement of the 15<sup>th</sup> August 1905 showed the following quantities for sale: —

District	Koti	Date of auction	Approximate quantity
Shimoga	Tirthahalli	14 November 1905	200 tons
do.	Sagar	18 " "	200 "
do.	Shimoga	22 " "	370 "
Kadur	Tarikere	25 " "	150 "
do.	Chikmagalur	28 " "	350 "
Hassan	Hassan	2 December "	200 "
Bangalore	Bangalore	6 " "	130 "
Mysore	Seringapatam	9 " "	250 "
do.	Hunsur	12 " "	450 "
Total			2300 tons,

<sup>1)</sup> Chemist and Druggist 68 (1906), 20.

<sup>2)</sup> Report October 1892, 41.

<sup>3)</sup> Report October 1904, 81.

whilst the auctions, as a matter of fact, are reported as showing about 100 tons more, i. e. in round figures 2400 tons. The disposition was very animated, partly at decidedly higher prices. We are informed that the latter are chiefly due to competition by native purchasers, who alone have taken off the market about 800 tons, i. e. one third of the entire quantity.

Under these conditions it is keenly felt that the prices of sandalwood oil should be raised proportionate to the values of the wood, but in view of the existing competition this will no doubt remain just at present a vain desire.

The *Madras Mail* of 15<sup>th</sup> September 1905 contained a long report from the Administration of Forests in Mysore, from which we see that no fewer than 28360 sandal-trees in the Mysore district, and 973 in the Hassan district, had to be uprooted, as having been attacked by the "spike"-disease. On the other hand, detailed experiments have proved that neither inoculation with diseased shoots, nor contact of the roots of healthy and diseased trees, can transmit the disease.

The Conservator states that the disease rarely occurs in districts where the other vegetation which exists alongside the sandal-trees is strong and healthy, which would support the theory that the spike-disease depends upon the degree of nutrition, and not upon the condition of the soil, but upon the neighbouring trees which, if of less duration of life than the sandal-trees, infect the latter. For this reason the disease does not appear to be of such importance as was originally believed.

Adulterations of sandalwood oil have again been observed on several occasions. Of particular interest is the case reported upon by E. Parry<sup>1</sup>), as we here become acquainted with a new and rather ingeniously selected adulterant. Parry namely found in a sandal oil originating from Germany, which was at once suspected on account of its low price, an adulteration with terpineol. The oil in question had the following properties:  $d_{15}^{\circ}$  0,970;  $n_D^{20}$  — 14°; esterified santalol 3,5%, apparent content of total santalol 93,5%; soluble in 5 vol. 70 per cent. alcohol.

By means of repeated fractional distillation *in vacuo* there was finally obtained a fraction consisting of about 5% of the oil used, which already by the odour revealed itself as terpineol, and which was identified as such by its physical properties and by the nitroso-chloride. Parry believes that terpineol was not the only substance added, but that the oil also contained West Indian Sandalwood oil, particularly certain readily soluble fractions of the latter richer in sesquiterpene alcohol. Parry intends following this matter up further.

<sup>1</sup>) Chemist and Druggist 68 (1906) 72, 211.

Another case mentioned by G. Wendt<sup>1)</sup> deals with the use of adulterated sandal oil for the manufacture of sandal oil capsules, an occurrence to which we have repeatedly drawn attention in our last Reports<sup>2)</sup>. The examination showed that the capsules in question contained not only an adulterated oil, but also nearly 30% less oil than was stated on the box. The manner of adulteration could not be ascertained. The manufacturer of the capsules contests the adulteration, but admitted that he had not used oil of best quality, with the explanation that only an oil had been guaranteed which would answer the requirements of the German Pharmacopœia IV, and which, as a matter of fact, the oil in question did answer.

We would add here that we have repeatedly observed, that inferior or adulterated sandalwood oils can pass the requirements of the German Pharmacopœia IV, and that it would therefore be advisable in a new edition of the Pharmacopœia at least to add the specification of the santalol content of the oil. We take this opportunity to point out once more, that in calculating the santalol content, we have taken as a basis the formula  $C_{15}H_{24}O$  which according to later investigations<sup>3)</sup> has been recognised as more correct. In an oil with a santalol content of 90% and higher, it gives an advantage of about 1% to the older formula  $C_{15}H_{26}O$ .<sup>4)</sup> We have hitherto always made our statements in accordance with the more correct formula, and will continue to do so. Possible differences may thus be explained.

**Sassafras Oil.** It is well known that sassafras oil is required to be soluble in every proportion in 90 per cent. alcohol. As we have repeatedly handled oils obtained from a reliable source, which showed a slightly lower solubility, we have distilled a sassafras oil ourselves — from the root-bark of *Sassafras officinale* Nees —, in order to test the correctness of the above-mentioned requirement. We then found, in agreement with our observations made on good commercial oils, that 1 to 2 vol. 90 per cent. alcohol are necessary to dissolve 1 vol. sassafras oil, although of course it cannot be denied that there are oils which are soluble in every proportion in 90 per cent. alcohol. The remaining properties of the distillate obtained by us were: bright yellow,  $d_{15^{\circ}} 1.075$ ,  $\alpha_D + 2^{\circ} 14'$ ; ester number 1.9. The yield of oil amounted to 3.25%.

**Savin Oil.** It is a well known fact that there exist considerable differences between the savin oils of German and British origin on the one hand, and the French distillate on the other, so that we have

<sup>1)</sup> Pharm. Zeitg. **50** (1905), 898.

<sup>2)</sup> Report October **1903**, 63; October **1904**, 83; April **1905**, 72.

<sup>3)</sup> Comp. Report October **1900**, 58.

<sup>4)</sup> Comp. the table in Report April **1903**, 106.

already on a previous occasion and in another place<sup>1)</sup> expressed the supposition that the French oil is only met with in commerce heavily adulterated with oil of turpentine. According to Umney and Bennett<sup>2)</sup> this supposition does not apply to all French oils, even if they possess properties differing from those of ordinary savin oil. The differences should rather be attributed to this, that we have here to deal with distillates of two different species of *Juniperus*. This at least the authors have observed in an oil obtained from a very reliable source, which corresponds well with the French commercial products, whilst differing markedly from ordinary savin oil. A further examination of the plant material showed that the oil did not originate at all from the leaves of *Juniperus sabina* L., but from the very similar *Juniperus phoenicea* L. indigenous to the Mediterranean countries. The properties of this oil were as follows:  $d_{15}^{20} 0,892$ ,  $\alpha_D + 4^\circ 30'$ , ester content 9,3 %, content of total sabinol 17,1 %, soluble in 5 vol. 90 per cent. alcohol. The oil is therefore lighter than ordinary savin oil, further, it has but a feeble rotation, and a decidedly lower alcohol content. Contrary to the German and British<sup>3)</sup> distillates it is rich in low-boiling constituents, 64 % passing over up to  $165^\circ$ , whilst the ordinary oils do not contain such low-boiling portions at all. Of constituents may be mentioned pinene, of which the oil contains a great deal, and also cadinene, and an aldehyde which, however, occurs in the oil in such small quantity that its identification was not possible.

As, according to Umney and Bennett, it is very probable that savin oil owes its physiological action in the first place to sabinol, it follows that the oil of *Juniperus phoenicea* L. which is less rich in sabinol, must be less active than the real oil of savin, and consequently cannot be a substitute of equal value for the latter.

For the rest Umney and Bennett do not supply any proof of the identity of the alcohol contained in the oil of *Juniperus phoenicea* L. with sabinol, which was all the more necessary as the botanical relationship between the mother plants does not by any means prove that the individual constituents must be identical.

**Solidago Oils.** From America we received two solidago oils. The one, designated merely as "oil of golden rod" had a pale yellow colour and a pleasant refreshing aroma. Its specific gravity was

<sup>1)</sup> Gildemeister and Hoffmann: "The Volatile Oils", pp. 274, 275.

<sup>2)</sup> Pharmac. Journal **75** (1905), 827.

<sup>3)</sup> For purposes of comparison Umney and Bennett also give the properties of a German and a British oil of savin. In this connection the exceptionally high rotation of the British oil which is said to be an authentic distillate, is worthy of note. Whilst the rotation usually fluctuates between  $+42^\circ$  and  $+60^\circ$ , the oil in question rotates  $+68^\circ$ . It further contains fewer high-boiling constituents than the German oil; the sabinol-content is normal.

0,8904 ( $15^{\circ}$ );  $\alpha_D - 15^{\circ} 34'$ ; ester number 34,2; ester number after acetylation 59,9. The oil does not form a clear solution with 10 vol. 90 per cent. alcohol, and even when 95 per cent. alcohol is used, the solution is only clear at the commencement; when more than 1,5 vol. alcohol is added, cloudiness occurs also in this case. The esters of the oil, judging from the odour, consist chiefly of bornyl acetate; from the ester number given above, a content of  $12\frac{0}{10}$  bornyl acetate is calculated.

We were unfortunately unable to ascertain whether the oil originates from *Solidago odora* Aiton, although this appears probable inasmuch as the distillates of this plant specially are called in America "*Oil of golden rod*".

The second sample received by us was derived from *Solidago nemoralis*. The bright olive-green oil had a peculiar odour, reminding somewhat of cypress oil. The constants were;  $d_{15^{\circ}} 0,8799$ ,  $\alpha_D - 23^{\circ} 10'$ , ester number 14,4, ester number after acetylation 38,2. The oil formed a cloudy solution in about 7 and more vol. 95 per cent. alcohol.

**Spearmint Oil.** The principal American distillers admit that with the high prices of the last few years, the consumption has fallen off, but not by far in the same proportion as the production which is said to be now only one fourth of what it used to be. For this reason a decline in the value is said to be out of the question.

In Thuringia the distillation ceased already years ago.

**Spike Oil.** The manufacturers in the South of France have received a useful lesson with this article. Whilst at the high tide of the lavender oil speculation as much as 12 francs were paid for spike oil, and even in October the market-price was 9,50 to 10 francs, there are now offers at 7 francs on the market, and it is very probable that we shall again arrive at normal conditions in the course of this year. In England there are large speculative stocks which are offered excitedly.

It appears advisable to refrain from large purchases until the situation has become clearer.

**Star-anise Oil.** Since the middle of last year the prices have advanced without interruption, and they are now about 1/- per lb. higher than at that time. The reason given, as far as Tonquin is concerned, is the bad star-anise harvest, and although no reports have been received from the neighbouring Chinese districts, the same may apply to that source of supply.

The export of Chinese oils of cassia and star-anise, according to Hong Kong export-lists, was in 1905

to the United Kingdom . . . .	526 cases
„ „ Continent . . . .	2283 „
<hr/>	
Total	2809 cases,

such a comparatively small quantity, that an error in the statistics may be assumed, inasmuch as possibly instead of cases, piculs of 2 cases are meant.

It is a well known fact that star-anise oil is obtained by distillation from the fruit of *Illicium verum*, a tree which is cultivated specially in the South of China and the North of Tonquin. In the course of researches made by Ph. Eberhardt<sup>1)</sup> with the view of improving the results of the cultivation, he also occupied himself with the internal morphology of the tree, and found that the mesophyll cells of the leaves are as rich in oil as the pericarpial cells of the fruit, in which the essential oil was specially deposited. In a trial-distillation Eberhardt received from 1 kilo leaves 200 drops of an oil with a strong odour. It has a somewhat lower solidifying point than that obtained from the fruit, congealing at 13°, against the latter at 16 to 18°. In order not to interfere with the development of the trees and the blossoms, it is best to collect particularly the old leaves only once every year, in the middle of the dry season, which is the most favourable time for this purpose. The leaves are cut up small and distilled so as to obtain the oil. By making use of this new method jointly with the old one, the annual production can, if not be doubled, at least be increased by two-thirds.

**Turpentine Oil.** We are indebted to the kindness of Mr. W. A. Lovegrove, Deputy Conservator of Forests at Naini Tal, British India, for a sample of the Indian turpentine derived from *Pinus longifolia* Roxb. and of the oil of turpentine obtained from it to which we have repeatedly referred in our last Reports. The ducts correspond in their properties with those observed by Rabenold. The balsam yielded on steam distillation, 19,3 % of a colourless oil, whilst a pale yellow brittle resin remained behind. The latter had the acid number 154,7, and an ester number of 8,8. The oil behaved as follows:  $d_{15}^{\circ} 0,8741$ ,  $\alpha_D + 0^{\circ} 43'$ , acid number 0, ester number 3,2, soluble in 7 to 8 and more vol. 90 per cent. alcohol. The oil sent to us from India had quite similar properties:  $d_{15}^{\circ} 0,8734$ ;  $\alpha_D + 3^{\circ} 13'$ ; acid number 1,9; ester number 1,3; soluble in 7,5 and more vol. 90 per cent. alcohol. In the distillation the following fractions were obtained: —

1.	165 to 170° (747 mm.)	33 %	$\alpha_D - 3^{\circ} 30'$
2.	170 " 175°	31 "	$\alpha_D + 0^{\circ} 40'$
3.	175 " 180°	14 "	$\alpha_D + 4^{\circ} 32'$
4.	above 180°	22 "	$\alpha_D + 16^{\circ} 22'$

<sup>1)</sup> Compt. rend. **142** (1906), 407.

<sup>2)</sup> Pharm. Review **23** (1905), 229. Report October **1905**, 68.

Although with the enormous wealth of forests of the United States of America, the question of a rapid exhaustion of the American turpentine production need not yet be considered, — in spite of the ruthless devastation of the forests by the largest and quickest possible extraction of turpentine as hitherto carried on — the American Administration of Forests has in recent years taken steps to arrest, by a careful and rational exploitation of the stock of conifers, the constantly spreading destruction of the forests. The attempts made to bring about some change in the hitherto universally applied method of collecting turpentine by the “box”-system for the purpose of obtaining large yields, with the view of preserving the resiniferous trees, have not remained without result. A new method, the “cup-and-gutter”-system, has now been proposed, which follows the lines of the system of turpentine production adopted in the South of France. A work by Charles Herty<sup>1)</sup>, published some time ago, deals in detail with the experiments made with the above-mentioned method. But before entering more fully into this matter, we wish to return with a few words to the “box”-system, and briefly describe this method and its disadvantages. According to this system, the first work, when spring approaches, is to cut a groove diagonally across the trunk of the tree, inclined towards the interior and ending in a hollow about 12" or 18" above the level of the ground. Now when with the warmer weather the sap of the tree begins to flow, the bark at both sides of the “box” or reservoir for the resin is peeled off up to a height of 8", in strips about 1" wide. The space between the box and the peeled-off strips is deprived of its bark down to the splint, and shortly afterwards the sap commences to flow down into the “box”. This work is continued every 2 or 3 weeks up to the end of October, and has the effect of constantly opening up fresh passages for the resin, which excrete their contents slowly into the “box”. With the advent of the autumn weather the secretion of resin becomes less and finally ceases entirely. After 4 or 5 years the same tree is no longer tapped. As already indicated, this “box”-system has many drawbacks, due both to the manner of obtaining the resin, and to the destruction of the tree by other influences. The cutting of the hollow causes the destruction of numerous resin-passages, and much resin is consequently lost. Moreover, the quality of the resin suffers from the fact that the readily-volatile portions of the sap of the tree evaporate, as they have to travel along a constantly increasing distance, owing to the tapping away being continued in an upward direction.

The new method which may be considered a combination of the “box”-system and the method generally employed in France, does

<sup>1)</sup> Dr. Charles Herty, A new method of turpentine orcharding; Washington, 1903.

away with most of the drawbacks mentioned above. In the first place, the cutting of a large hollow in the trunk is obviated. Its place is taken by a receptacle which is suspended from a nail in the trunk. As in the "box"-system, here also the first work is cutting strips in the bark and the splint, and as the work proceeds the space above the receptacle is gradually cleared of bark. In order to let the exuding resin collect in the earthenware pots or vessels placed below, two strips or gutters of galvanised sheet iron about 2" wide by 6" to 12" long are employed. These are placed in grooves cut into the trunk with a broad axe in such manner, that each of the two cuts forms an angle of  $60^\circ$  with the longitudinal axis of the tree, and the two together therefore form an angle of  $120^\circ$  open at the top. The two gutters however are not placed at the same height, but one about 1" or 2" above the other, so that the resin flowing along the upper gutter only passes the other one when flowing down, and then passing through the lower gutter reaches the vessel placed below the latter. When the cuts in the trunk and the peeling of the bark is continued in an upward direction, the gutters and the vessel are also moved upwards. In stouter trees containing more resin, several such vessels can of course be placed around the tree. The new method is still being tried further, but it can be foreseen that it guarantees a more rational output of the trees than is possible with the "box"-system.

Utz<sup>1)</sup> makes some further communications on the examination of oil of turpentine and substitutes of oil of turpentine. He determined the iodine number<sup>2)</sup> of various turpentine oils and pine tar oils, and found somewhat considerable differences in the values; he draws the conclusion that the iodine number has little importance for the analysis of turpentine oil, as according to experiments made, the iodine numbers vary considerably according to the manner of keeping the oils. Utz has confirmed the colour reaction indicated by Valenta for pinolin. He also found that pinolin, in the treatment with concentrated and fuming sulphuric acid, shows a larger separation than the different turpentine oils, whilst the refraction of the oil separated off is lower than that of oil of turpentine.

Vaubel<sup>3)</sup> recommends for the valuation of turpentine oils, the determination of the bromine number, which the author accomplishes

<sup>1)</sup> Chem. Rev. Fett- und Harzindustrie **12** (1905), 231. Accord. to Chem. Centralbl. **1905**, II, 1393.

<sup>2)</sup> The iodine numbers ascertained by Utz for turpentine oil (223.5 to 331.6) lie between the values found earlier by Worstall on the one hand, and by Harvey on the other, and they afford a fresh proof of how much depends here on the conditions of the test. Comp. Report October **1904**, 85.

<sup>3)</sup> According to a paper. Zeitschr. f. öff. Chem. **11** (1905), 429. Acc. to Chem. Centralbl. **1906**, I, 199.

as follows: 1 to 2 grams oil are dissolved in 100 cc. glacial acetic acid, or better chloroform<sup>1)</sup>, 5 g. potassium bromide and 20 cc. fuming hydrochloric acid are added, and next enough of a titrated solution of potassium bromate to cause a permanent bromine reaction. The bromine numbers found by Vaubel agree well with the iodine numbers found by Worstall. On the other hand, Holde considers the specific gravity of the turpentine oils, and Herzfeld their behaviour towards concentrated and fuming sulphuric acid, as better standards for valueing than the bromine number.

**Wintergreen Oil.** The last shipments made by our New York branch have still been invoiced at the old price, but for future consignments the prospects are higher prices. As the present value is abnormally low, the timely purchase of supplies should not be delayed.

Siro Grimaldi<sup>2)</sup> has detected salicylic acid (which most probably originates from the action of a ferment on a glucoside as methyl ester of salicylic acid) in various parts of plants, as for example in the agriots which in each kilogr. fruit contains 0,1 to at most 0,45 to 0,5 mg. salicylic acid; further in the berries of *Vitis labrusca* Linn. and in those of *Rubus idaeus* Linn., especially in the raspberries of Monte Amiata. The author detected this acid in the benzene or ether extract of the parts of the plant in question, by means of the ferric chloride reaction, and by conversion of the acid into ammonium picrate when submitted to the action of aqueous nitric acid and subsequently of ammonia.

**Wormwood Oil.** Over-production in the South of France and Algeria has depressed the prices as never before, whilst there is an excellent selection of qualities. The competition of the American oil has been paralysed by the abnormal state of the price.

**Ylang-Ylang Oil.** Although the consignments of the "Sartorius" brand were again more abundant last year, the demand could only be met with great difficulty. According to the most recent reports from Manila, dating from the end of January, there was then a scarcity of blossoms, and the distillation had been interrupted in consequence; but this is now probably past, as a shipment has meanwhile been advised by cable. Our friends in Manila make every possible effort to increase the production to such an extent, that the consumption can always be fully satisfied. According to official consular reports, the value of ylang-ylang oil exported from Manila in the year 1904/1905 amounted to 100349 dollars, i. e. about 300 dollars less than in the two preceding years.

<sup>1)</sup> Comp. also Pharm. Ztg. **51** (1906), 257.

<sup>2)</sup> Staz. sperim. agrar. ital. **38** (1905), 28 to 21. Accord. to Chem. Centralbl. **1905**, II., 1503.

## Novelties.

Some new oils obtained from the Imperial Biologico-Agricultural Institute of Amani (German East Africa) have been examined by R. Schmidt and K. Weilingner<sup>1</sup>).

**Oil from the bark of *Ocotea usambarensis* Engl.** The bark of this tree which belongs to the Lauraceæ and which is found in fairly large numbers in the primeval forests, yielded 0,15 % essential oil of the following properties: boiling point at 10 mm. pressure 50 to 160°,  $d_{20} 0,913$ ,  $n_D 1,476$ ,  $\alpha_D 20^\circ - 11^\circ 12'$ , acid number 1,2, ester number 12,5; content of free alcohols ( $C_{10}H_{18}O$ ) 4,5%; free from sulphur and nitrogen. By shaking the oil with potash liquor, 0,3% of a phenol not further identified were obtained, and by means of bisulphite liquor 1% myristinic aldehyde which was identified by its semicarbazone (melting point 100 to 101°) and by oxidation into myristinic acid. When the oil was shaken with hydrazin benzenesulphoacid, a very small quantity of a ketone was obtained, whose semicarbazone melted at 197°. The oil further contained 40% cineol (identified by the iodol compound), 40% l-terpineol (boiling point 100 to 110° at 12 mm. pressure;  $d_{20} 0,922$ ;  $n_D 1,484$ ;  $\alpha_D - 37^\circ 6'$ ) which was detected by conversion into dipentene dihydrochloride (melting point 46°), and 10% sesquiterpene  $C_{15}H_{24}$  (boiling point 136 to 142° at 12 mm pressure:  $d_{20} 0,915$ ,  $n_D 1,535$ ;  $\alpha_D + 7^\circ 46'$ ) whose dihydrochloride (melting point 116 to 117°) is not identical with cadinene hydrochloride.

**Oil of *Piper Volkensii* C. D. C.** The leaves of this plant which is found in considerable numbers in the damp forests of Usambara, yielded 0,3 % essential oil of a bright-brown colour and a powerful pleasant odour, which had the following properties: boiling point 90 to 175° at 12 mm. pressure,  $d_{20} 0,934$ ,  $n_D 1,5017$ ,  $\alpha_D - 8^\circ 24'$ , ester-content 6% geranyl acetate, content of free alcohols 14%  $C_{10}H_{18}O$ . By means of phthalic acid anhydride there were abstracted from the oil 4% of a primary alcohol (possibly citronellol). The principal fraction (70%) of the saponified oil boiled at 135° to 148°, at 15 mm. pressure, and absorbed bromine with formation of a bromide  $C_{11}H_{12}O_3Br_2$  (melting point 122°), which was reconverted into the body  $C_{11}H_{12}O_3$  by reduction with zinc dust and glacial acetic acid. As this product contains 14,1% methoxyl, the authors believe that they may possibly have to deal with a methoxylized safrol. In addition to this, they detected in the principal fraction the sesquiterpene limene found by Burgess and Page in oil of

<sup>1</sup>) Berl. Berichte 39 (1906), 652.

limette. Like the latter, the sesquiterpene found absorbs 3 molecules hydrochloric acid (melting point of the hydrochloride  $79$  to  $80^{\circ}$ ) and 6 atoms bromine (melting point of the bromide  $154^{\circ}$ ).

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## New Pharmacopœias.

In our last Report we have already published a summary of the requirements specified by the new American Pharmacopœia for the essential oils admitted to it, and we stated at the same time that a discussion of the details was at that moment not possible, but would follow in the present Report. In the meantime, two more new Pharmacopœias have appeared, namely the seventh edition of the Spanish Pharmacopœia which has recently come into force, and the eighth edition of the Austrian Pharmacopœia which takes effect from the 1<sup>st</sup> July 1906. As on previous occasions, we will in the following pages briefly quote the requirements specified in the various Pharmacopœias for the essential oils, and in each case discuss whatever may need supplementing or correcting, as that will be the best way of preventing any misunderstandings which might arise in judging individual oils on the basis of the Pharmacopœia in question.

The new (IV.) Dutch Pharmacopœia unfortunately only reached us after the editorial portion of this Report was closed, and we therefore reserve a discussion of same for the next October Report.

### American Pharmacopœia.

(The Pharmacopœia of the United States of America,  
8<sup>th</sup> decennial revision).

The new edition of the American Pharmacopœia has deservedly met with general approbation. There are everywhere evidences of a serious effort to make the widest possible use of the achievements of Science; particularly this is the case in the directions for testing. This also applies especially to the essential oils, which are mostly described in detail in such manner that the American Pharmacopœia may in this respect be characterized to a certain extent as typical. This favourable opinion of the whole does not preclude that some statements made in the Pharmacopœia are not correct, and also that several directions for testing call for criticism. For the sake of expediency, we will first of all discuss in a connected form, the specific gravities specified by the Pharmacopœia, and then deal with the oils themselves.

As already mentioned by us in our Report of October 1905, p. 74, the new American Pharmacopœia does not indicate the specific

gravities of the essential oils, as is usually done, at  $\frac{15^{\circ}}{15^{\circ}}$ , but at  $\frac{25^{\circ}}{25^{\circ}}$ . This rule has induced us to determine for all essential oils included in the Pharmacopœia, the differences existing between the specific gravities at  $\frac{15^{\circ}}{15^{\circ}}$  and at  $\frac{25^{\circ}}{25^{\circ}}$ , so as to form an opinion whether and in how far the limits of value given in the Pharmacopœia agree with those obtained at  $15^{\circ}$ . We have here in several cases found more or less considerable differences. For the purpose of a better review we have combined the results obtained in a tabulated form (p. 71). The limits of value given in the American Pharmacopœia, which do not agree with ours, are printed in heavy type. These limits printed thus cannot and should not in our opinion be accepted as such, for they are inconsistent with the values fixed for  $15^{\circ}$ , and are consequently incorrect. Differences of 1 in the third decimal figure have been left out of account, as they lie within the limits of error. We would still mention that the differences between the specific gravities determined at  $\frac{15^{\circ}}{15^{\circ}}$  and at  $\frac{25^{\circ}}{25^{\circ}}$ , as given by us, agree well on the whole with those ascertained previously by Schreiner and Downer<sup>1)</sup>, and also that the average value of these differences is the same as that found by those authors, viz. 0,00064 per degree of temperature.

Of alcohols, the American Pharmacopœia recognises a strong alcohol of 94,9 per cent. by volume (Alcohol), and a weak one of 48,9 per cent. by volume (Alcohol dilutum). In the following page the former is designated simply as "alcohol."

**Anise Oil** (*Oleum anisi*). Colourless or faintly yellow:  $d_{25^{\circ}}$  0,973 to 0,985<sup>1)</sup>;  $\alpha_{D25^{\circ}}$  —  $2^{\circ}$ <sup>2)</sup>; solidifying point not below  $+15^{\circ}$ ; soluble in an equal volume alcohol and in 5 vol. 90 per cent. alcohol.

<sup>1)</sup> The upper limit of value should be 0,988, as otherwise especially the oil richest in anethol, and consequently the most valuable anise oils, could not be used. Comp. also the table (p. 71).

<sup>2)</sup> This should read: up to —  $2^{\circ}$ .

**Benzaldehyde** (*Benzaldehydum*). Colourless liquid, strongly refractive, with at least 85% pure benzaldehyde<sup>1)</sup>;  $d_{25^{\circ}}$  about 1,045;  $\alpha_D \pm 0^{\circ}$ ; boiling point 179 to 180°; soluble in alcohol in every proportion; test for absence of chlorinated products.

<sup>1)</sup> According to the method of determination by means of neutral sodium sulphite indicated by the Pharmacopœia, we found it impossible to obtain even approximately satisfactory results; for this reason, we greatly doubt the usefulness of this method.

**Bitter Almond Oil** (*Oleum amygdalæ amaræ*). Colourless or yellow; content of benzaldehyde at least 85%<sup>1)</sup>; content of hydrocyanic acid between 2 and 4%<sup>2)</sup>;  $d_{25^{\circ}}$  1,045 to 1,060<sup>3)</sup>;  $\alpha_D \pm 0^{\circ}$ <sup>4)</sup>.

<sup>1)</sup> Pharm. Archives 4 (1901), 165. Report April 1902, 80.

Table.

	$d_{15}^{15}$	$d_{25}^{25}$	Difference	Limits of value at $\frac{15}{15}$	Limits of value at $\frac{25}{25}$	American Pharma- copœia $\frac{25}{25}$
Cinnamon Oil . . . . .	0,9915	0,9855	0,0060	0,984—0,994	0,978—0,988	0,975—0,985
Cinnamaldehyde . . . .	1,0584	1,0515	0,0069	1,050—1,055	1,043—1,048	about 1,045
Coconut Almond Oil . .	1,0655	1,0587	0,0068	1,045—1,070	1,038—1,063	1,045—1,060
Cajuput Oil . . . . .	0,9215	0,9151	0,0064	0,919—0,930	0,913—0,924	0,915—0,925
Cassia Oil . . . . .	0,9080	0,9023	0,0057	0,905—0,915	0,899—0,909	0,905—0,915
Cassia Oil, rect. . . .	1,0551	1,0489	0,0062	1,053—1,065	1,047—1,059	1,045—1,055
Cenopodium Oil . . . .	0,9769	0,9706	0,0063	?		0,965—0,985
Cinamic Aldehyde . . .	1,0560	1,0504	0,0056	1,054—1,058	1,048—1,052	about 1,047
Clove Oil . . . . .	1,0487	1,0422	0,0065	1,040—1,060	1,033—1,053	1,040—1,060
Copaiba Oil . . . . .	0,9056	0,9002	0,0054	0,900—0,920	0,895—0,915	0,895—0,905
Coriander Oil . . . . .	0,8739	0,8672	0,0067	0,870—0,880	0,863—0,873	0,863—0,878
Cubeb Oil . . . . .	0,9214	0,9159	0,0055	0,915—0,930	0,909—0,924	0,905—0,925
Ciguatera Oil . . . . .	0,8865	0,8803	0,0062	0,850—0,870	0,844—0,864	0,845—0,865
Calyptol . . . . .	0,9294	0,9227	0,0067	0,928—0,930	0,921—0,923	0,925
Calyptus Oil . . . . .	0,9146	0,9083	0,0063	0,910—0,930	0,904—0,924	0,905—0,925
Caryophyllol . . . . .	1,0716	1,0650	0,0066	1,071—1,074	1,064—1,067	1,072—1,074
Cinnamon Oil . . . . .	0,9715	0,9653	0,0062	0,965—0,977	0,959—0,971	0,953—0,973
Cedroma Oil (Oil of Sassafras. Pennyroyal)	0,9331	0,9271	0,0060	0,925—0,940	0,919—0,934	0,920—0,935
Oil of Juniper berries .	0,8655	0,8593	0,0062	0,860—0,885	0,854—0,879	0,860—0,880
Citron Oil . . . . .	0,8864	0,8797	0,0067	0,882—0,895	0,875—0,888	0,880—0,892
Common Oil . . . . .	0,8585	0,8527	0,0058	0,857—0,861	0,851—0,855	0,851—0,855
Mustard Oil . . . . .	1,0200	1,0120	0,0080	1,016—1,025	1,008—1,017	1,013—1,020
Nutmeg Oil . . . . .	0,9037	0,8972	0,0065	0,870—0,930	0,864—0,924	0,862—0,910
Peppermint Oil . . . .	0,9060	0,9006	0,0054	0,900—0,920	0,895—0,915	0,894—0,914
Peppermint Oil . . . .	1,0440	1,0372	0,0068	1,025—1,055	1,018—1,048	1,033—1,048
Rose Oil <sup>1)</sup> . . . . .		0,8625			0,854—0,867	0,855—0,865
Rosemary Oil . . . . .	0,9077	0,9011	0,0066	0,900—0,920	0,893—0,913	0,894—0,912
Sassafras Oil . . . . .	1,1054	1,0985	0,0069	1,105—1,107	1,098—1,100	1,105—1,106
Sandalwood Oil . . . .	0,9782	0,9735	0,0047	0,975—0,985	0,970—0,980	0,965—0,975
Sassafras Oil . . . . .	1,0807	1,0740	0,0067	1,070—1,082	1,063—1,075	1,065—1,075
Savin Oil . . . . .	0,9208	0,9150	0,0058	0,910—0,930	0,904—0,924	0,903—0,923
Spearmint Oil . . . . .	0,9352	0,9290	0,0062	0,920—0,940	0,914—0,934	0,914—0,934
Sweet Orange Oil . . .	0,8509	0,8452	0,0057	0,849—0,853	0,843—0,847	0,842—0,846
Thyme Oil, white . . . .	0,9068	0,9007	0,0061	0,900—0,935	0,894—0,929	0,900—0,930
Turpentine Oil . . . . .	0,8682	0,8616	0,0066	0,865—0,875	0,858—0,868	0,860—0,870
Turpentine Oil, rect. .	0,8708	0,8643	0,0065	0,860—0,871	0,853—0,864	0,860—0,865
Wintergreen Oil:						
from <i>Betula</i>						
<i>lenta</i> L. . . . .	1,1870	1,1794	0,0076	1,180—1,188	1,172—1,180	1,172—1,180
from <i>Gaultheria</i>						
<i>procumbens</i> L. . . .	1,1864	1,1788	0,0076	1,180—1,188	1,172—1,180	1,172—1,180
Artificial . . . . .	1,1896	1,1817	0,0079	1,185—1,190	1,177—1,182	1,180—1,185

<sup>1)</sup> The limits of value given for rose oil were based upon those in force for  $\frac{30}{15}$ .

boiling point about  $180^{\circ}$ ; soluble in every proportion in alcohol, also in an equal volume 70 per cent. alcohol<sup>5)</sup>; test for absence of chlorinated products.

<sup>1)</sup> Comp. note under benzaldehyde.

<sup>2)</sup> Such a content of hydrocyanic acid cannot always be guaranteed.

<sup>3)</sup> The specific gravity given is for a temperature of  $15^{\circ}$ , but it should be taken into consideration that even in the case of absolutely normal oils, it often amounts to 1,070; for  $25^{\circ}$  the following figures apply: 1,038 to 1,063 (comp. table).

<sup>4)</sup> Occasionally a feeble optical activity is also observed.

<sup>5)</sup> Of 70 per cent. alcohol, 1 to 2 volumes are required to dissolve the oil.

**Cajeput Oil** (*Oleum cajuputi*). Colourless or greenish; cineol-content at least 55 per cent. by volume<sup>1)</sup>;  $d_{25^{\circ}}$  0,915 to 0,925<sup>2)</sup>; laevorotatory,  $\alpha_{D25^{\circ}}$  not above  $-2^{\circ}$ <sup>3)</sup>; soluble in every proportion in alcohol, also in 1 part 80 per cent. alcohol.

<sup>1)</sup> The estimation of cineol is accomplished by means of phosphoric acid in the following manner: 10 cc. oil are dissolved in 50 cc. petroleum ether, and to the well cooled solution (freezing mixture) is gradually added, whilst stirring, concentrated phosphoric acid, until the white compound separating off acquires a yellowish (or reddish) shade. The crystalline mass is then filtered off with a suction pump, washed with petroleum ether, pressed to remove the last liquid portions, and decomposed with water. The cineol separated off is estimated volumetrically and the percentage calculated.

We have again convinced ourselves by estimations of mixtures of a known cineol-content, that this method does not always give reliable results. This applies specially to oils less rich in cineol; for example, in mixtures of 50 per cent., the content of cineol found was up to 8 per cent. too little, although we endeavoured by different small improvements, to avoid sources of error as much as possible. For this reason, the cineol-estimations can only lay claim to approximate accuracy.

<sup>2)</sup> As lower limit of value, 0,913 is to be recommended (comp. table).

<sup>3)</sup> With pure distillates, we have observed rotations up to  $-2^{\circ}40'$ .

**Camphor** (*Camphora*). White, transparent mass;  $d_{25^{\circ}}$  0,990;  $\alpha_D$  to the right; melting point  $175^{\circ}$ ; boiling point  $204^{\circ}$ .

**Caraway Oil** (*Oleum cari*). Colourless or pale yellow;  $d_{25^{\circ}}$  0,905 to 0,915<sup>1)</sup>;  $\alpha_{D25^{\circ}}$   $+70$  to  $+80^{\circ}$ ; soluble in an equal volume alcohol, and in 3 to 10 volumes 80 per cent. alcohol.

<sup>1)</sup> The specific gravity given applies to a temperature of  $15^{\circ}$ ; it should read:  $d_{25^{\circ}}$  0,899 to 0,909 (comp. table).

**Cassia Oil**<sup>1)</sup> (*Oleum cinnamomi*). Yellowish or brownish; content of cinnamic aldehyde at least 75 per cent. by volume;  $d_{25^{\circ}}$  1,045 to 1,055<sup>2)</sup>;  $\alpha_{25^{\circ}}$  between  $-1^{\circ}$  and  $+1^{\circ}$ ; soluble in 2 volumes 70 per cent. alcphol.

<sup>1)</sup> Only the rectified oil answers the requirements given.

<sup>2)</sup> The upper limit of value given is slightly too low; it should be 1,059 (comp. table).

**Chenopodium Oil** (*Oleum chenopodii*). Colourless or yellow;  $d_{25^{\circ}}$  about 0,965 to 0,985<sup>1)</sup>; laevorotatory,  $\alpha_{D25^{\circ}}$  not above  $-5^{\circ}$ <sup>2)</sup>; soluble in 5 volumes 70 per cent. alcohol.

<sup>1)</sup> The Pharmacopœia here quite correctly only requires approximate values, as oil of chenopodium is extremely variable owing to its content of a constituent which decomposes very readily; this also causes changes in the specific gravity.

<sup>2)</sup> We have observed with good commercial oils, rotations up to  $-6^{\circ}$ .

**Cinnamic aldehyde** (*Cinnaldehydum*). Colourless<sup>1)</sup>; containing at least 95% pure cinnamic aldehyde;  $d_{25^{\circ}}$  about 1,047<sup>2)</sup>;  $\alpha_D \pm 0^{\circ}$ ; boils about  $250^{\circ}$  with decomposition; solidifies in a freezing mixture and melts again at  $-7,5^{\circ}$ ; soluble in every proportion in alcohol.

<sup>1)</sup> Cinnamic aldehyde is not colourless, but bright yellow.

<sup>2)</sup> The statement of the specific gravity is not correct, it should read:  $d_{25^{\circ}}$  1,048 to 1,052 (comp. table).

**Clove Oil** (*Oleum caryophylli*). Colourless or pale yellow; eugenol-content at least 80 per cent. by volume;  $d_{25^{\circ}}$  1,040 to 1,060<sup>1)</sup>; soluble in an equal volume alcohol, and in about 2 volumes 70 per cent. alcohol.

<sup>1)</sup> As oils with a eugenol-content down to 80% are admitted, the lower limit of the specific gravity should be reduced to 1,033 (comp. table).

**Copaiba Oil** (*Oleum copaibæ*). Colourless or pale yellow,  $d_{25^{\circ}}$  0,895 to 0,905<sup>1)</sup>;  $\alpha_D$  to the left; soluble in 2 vol. alcohol<sup>2)</sup>.

<sup>1)</sup> The specific gravity at  $15^{\circ}$  amounts to up to 0,918, as we have recently observed with one of our own distillates (comp. Report April 1905, 25). The specific gravity mentioned corresponds to the value 0,915 at  $25^{\circ}$  (see table).

<sup>2)</sup> On the strength of observations with authentic material we are in a position to state that 1 vol. copaiba oil requires 5 to 10 vol. 95 per cent. alcohol to form a solution. See Report April 1905, 25.

**Coriander Oil** (*Oleum coriandri*). Colourless or faintly yellow;  $d_{25^{\circ}}$  0,863 to 0,878;  $\alpha_{D25^{\circ}}$   $+7$  to  $+14^{\circ}$ ; soluble in 3 volumes 70 per cent. alcohol; in 80 and 90 per cent. alcohol soluble in every proportion.

**Oil of Cubebs** (*Oleum cubebæ*). Colourless, pale green, or yellow;  $d_{25^{\circ}}$  0,905 to 0,925;  $\alpha_{D25^{\circ}}$   $-25$  to  $-40^{\circ}$ .

**Erigeron Oil** (*Oleum erigerontis*). Faintly yellow;  $d_{25^{\circ}}$  0,845 to 0,865;  $\alpha_{D25^{\circ}}$  about  $+50^{\circ}$ ; soluble in an equal volume alcohol.

**Eucalyptol**. Colourless;  $d_{25^{\circ}}$  0,925<sup>1)</sup>;  $\alpha_D \pm 0^{\circ}$ ; boiling point 176 to  $177^{\circ}$ ; solidifies on cooling into needle-shaped crystals, which melt at  $-1^{\circ}$ ; soluble in every proportion in alcohol.

<sup>1)</sup> The specific gravity at  $25^{\circ}$  is not 0,925, but fluctuates between 0,921 and 0,923 (comp. table).

<sup>2)</sup> Solidification has to be started in case of need by rubbing a glass rod on the wall of the vessel.

**Eucalyptus Oil** (*Oleum eucalypti*). Colourless or faintly yellow<sup>1)</sup>; cineol-content at least 50 per cent. by volume<sup>2)</sup>;  $d_{25^{\circ}}$  0,905 to 0,925;  $\alpha_D 25^{\circ}$  not above  $+10^{\circ}$ ; soluble in every proportion in alcohol and in 3 volumes 70 per cent. alcohol; free from phellandrene.

<sup>1)</sup> The oil has occasionally also a greenish shade.

<sup>2)</sup> With regard to the cineol-estimation, compare what has been said under cajeput oil.

**Eugenol.** Colourless or faintly yellow:  $d_{25}^{\circ}$  1,072 to 1,074<sup>1)</sup>;  $\alpha_D \pm 0^{\circ}$ ; boiling point 251 to 253<sup>o</sup>; soluble in every proportion in alcohol, and in 2 parts 70 per cent. alcohol.

<sup>1)</sup> These figures apply to 15<sup>o</sup>; at 25<sup>o</sup> the specific gravity lies between 1,064 and 1,067 (comp. table).

**Fennel Oil** (*Oleum feniculi*). Colourless or faintly yellow;  $d_{25}^{\circ}$  0,953 to 0,973; solidification point not below + 5<sup>o</sup><sup>1)</sup>; soluble in an equal volume alcohol, likewise in 10 volumes or less 80 per cent. alcohol.

<sup>1)</sup> Solidification must in case of need be introduced by inoculation with a small crystal of anethol. The lowest limit of the solidification point might suitably be + 4<sup>o</sup>, as in commercial products it is usually found between + 4 and + 6<sup>o</sup>.

**Oil of Hedeoma or American pennyroyal** (*Oleum hedeomæ*). Faintly yellow:  $d_{25}^{\circ}$  0,925 to 0,935;  $\alpha_D$  25<sup>o</sup> from about + 18 to + 22<sup>o</sup>; soluble in 2 and more vol. 70 per cent. alcohol.

**Oil of Juniper berries** (*Oleum juniperi*). Colourless, faintly green or yellow;  $d_{25}^{\circ}$  0,860 to 0,880<sup>1)</sup>; soluble in 10 volumes 90 per cent. alcohol<sup>2)</sup>.

<sup>1)</sup> Oil of juniper berries is also frequently lighter; a lowest limit of 0,854 would be more suitable (comp. table).

<sup>2)</sup> The specification of solubility is mostly only answered by quite fresh distillates; even when kept in a rational manner the solubility of oil of juniper berries diminishes rapidly.

**Lavender Oil** (*Oleum lavandulae florum*). Colourless or yellow;  $d_{25}^{\circ}$  0,880 to 0,892<sup>1)</sup>; soluble in 3 vol. 70 per cent. alcohol.

<sup>1)</sup> The lower limit of the specific gravity is not correct; it should read: 0,875 (comp. table).

**Lemon Oil** (*Oleum limonis*). Faintly yellow, citral-content not less than 4 0/0<sup>1)</sup>;  $d_{25}^{\circ}$  0,851 to 0,855;  $\alpha_{D25}^{\circ}$  not below + 60<sup>o</sup><sup>2)</sup>;  $\alpha_D$  of the first 10 0/0 of the distillate may only differ 2<sup>o</sup> from the angle of rotation of the oil<sup>3)</sup>.

<sup>1)</sup> The citral-determination is made by Sadtler's method (comp. Reports April 1904, 47 and October 1904, 119) with this extension, that in addition to the actual test also a "blind" test without oil is made; this is no doubt a decided step in advance as in this manner the end of the reaction can be observed or approximated somewhat better, but in the tests made by us we have again come to the conclusion, that a really exact determination is not possible even in this manner, and for this reason we must continue, as before, to characterize the method as unreliable.

<sup>2)</sup> The rotation of lemon oil varies considerably with the temperature; the one given above would correspond to a rotation of 60° 41' at the usual observation temperature of 20°. As pure oils are frequently met with, with a rotation down to 58°, and as most oils rotate about 60°, the above requirement of the Pharm. copœia does not take the actual facts sufficiently into account.

<sup>3)</sup> According to our experience, the difference in pure oils frequently amounts to up to 5°.

**Menthol.** Colourless needle-shaped or prismatic crystals; melting point  $43^{\circ}$ ; boiling point  $212^{\circ}$ ; alcoholic solution neutral and lævotatory.

**Mustard Oil** (*Oleum sinapis volatile*). Colourless or faintly yellow;  $d_{25^{\circ}}$  1,013 to 1,020<sup>1)</sup>; boiling point  $148$  to  $152^{\circ}$ ; lowest content of allyl isothiocyanate  $92\%$ <sup>2)</sup>; soluble in every proportion in alcohol.

1) The lower limit is given too high, and should be 1,008 (comp. table).

2) With regard to the determination, comp. the present Report p. 45.

**Nutmeg Oil** (*Oleum myristicæ*). Colourless or faintly yellow;  $d_{25^{\circ}}$  0,862 to 0,910<sup>1)</sup>;  $\alpha_{D25^{\circ}}$   $+14$  to  $+28^{\circ}$ <sup>2)</sup>; soluble in an equal vol. alcohol, and in 3 vol. 90 per cent. alcohol. When 2 to 3 cc. oil are evaporated, no crystallising residue should remain behind.

1) The upper limit is given too low and must be increased to 0,924, as otherwise just the oil from the best material is excluded from medicinal use. Comp. Report October 1904, 65; see also table.

2) We have observed in our own distillates from nutmeg of best quality, rotations down to  $+7^{\circ}52'$ . Comp. Report October 1904, 65.

**Peppermint Oil**<sup>1)</sup> (*Oleum menthæ piperitæ*). Colourless<sup>2)</sup>;  $d_{25^{\circ}}$  0,894 to 0,914;  $\alpha_{D25^{\circ}}$   $-25$  to  $-33^{\circ}$ ; ester (menthyl acetate) at least  $8\%$ <sup>3)</sup>; total menthol (free and esterified) at least  $50\%$ ; soluble in an equal vol. alcohol; the solution in 4 volumes 70 per cent. alcohol may at most show a feeble opalescence.

1) The requirements given for peppermint oil are partly contradictory, so that it is not clear whether the oil from the State of New York ("Wayne County Oil") or that from Michigan ("Western Oil") is to be the official oil. Whereas the rotation applies chiefly to the first-named oil (Michigan oil rotates between  $-18$  and  $-29^{\circ}$ ), the requirements of solubility exclude the former as the New York oil is not soluble in 70 per cent. alcohol. It is difficult to understand why both oils are not admitted.

2) Peppermint oil is not always colourless, but sometimes yellowish or greenish yellow.

3) The ester-content is frequently lower; we have observed in authentic oils down to  $4\%$ .

**Pimenta Oil** (*Oleum pimentæ*). Colourless, yellow, or reddish; eugenol-content at least 65 per cent. by volume;  $d_{25^{\circ}}$  1,033 to 1,048<sup>1)</sup>; soluble in every proportion in 90 per cent. alcohol and also in 2 vol. 70 per cent. alcohol.

1) The lower limit of value is given too high, and should be 1,018. Comp. table; see also German Report April 1899, 39.

**Rose Oil** (*Oleum rosæ*). Faintly yellow;  $d_{25^{\circ}}$  0,855 to 0,865<sup>1)</sup>; saponification number 10 to 17<sup>2)</sup>; solidifying point between  $18$  and  $22^{\circ}$ <sup>3)</sup>.

1) The upper limit is given too low, and should be 0,867 (comp. table).

2) We have observed in pure oils saponification numbers between 8,5 and 19.

3) As upper limit for the solidifying point  $23,5^{\circ}$  might be recommended.

**Rosemary Oil** (*Oleum rosmarini*). Colourless or faintly yellow;  $d_{25}^{\circ}$  0,894 to 0,912;  $\alpha_{D25}^{\circ}$  not above  $+15^{\circ}$ ; the first 10% of the distillate must also be dextrorotatory. Ester-content (calculated as bornyl acetate) at least 5%; total borneol at least 15%<sup>1)</sup>; soluble in 0,5 and more vol. 90 per cent. alcohol, and also in 2 to 10 vol. 80 per cent. alcohol.

<sup>1)</sup> These requirements cannot be upheld; we have observed in good oils an ester-content down to 1,2%, and a total content of borneol down to about 10%.

**Safrol** (*Safrolum*). Colourless or faintly yellow;  $d_{25}^{\circ}$  1,105 to 1,106<sup>1)</sup>;  $\alpha_D \pm 0^{\circ}$ ; boiling point about  $233^{\circ}$ ; when cooled to  $-20^{\circ}$  or below, is solidifies into a crystalline mass which does not melt below  $+11^{\circ}$ ; soluble in about an equal volume alcohol, and in about 30 volumes 70 per cent. alcohol.

<sup>1)</sup> The data of the specific gravity approximately correspond to those determined for  $15^{\circ}$ : 1,105 to 1,107; at  $25^{\circ}$  the specific gravity varies between 1,098 and 1,100 (comp. table).

**Sandalwood Oil, East Indian** (*Oleum santali*). Faintly yellow;  $d_{25}^{\circ}$  0,965 to 0,975<sup>1)</sup>;  $\alpha_{D25}^{\circ}$   $-16$  to  $-20^{\circ}$ ; santalol-content not below 90%<sup>2)</sup>; soluble in 5 vol. 70 per cent. alcohol.

<sup>1)</sup> The upper limit of value is too low, it should be 0,980 (comp. table).

<sup>2)</sup> It is to be regretted that the Pharmacopœia bases its calculation of santalol on the formula  $C_{15}H_{26}O$ . We have already repeatedly pointed out that according to recent investigations the formula  $C_{15}H_{24}O$  is undoubtedly more correct. Comp. Report October 1900, 58, and the present Report p. 60. The lowest content of 90% mentioned above, and based upon  $C_{15}H_{26}O$ , corresponds to a minimum of 89,2% calculated on  $C_{15}H_{24}O$ .

**Sassafras Oil** (*Oleum sassafras*). Yellow or reddish yellow;  $d_{25}^{\circ}$  1,065 to 1,075<sup>1)</sup>;  $\alpha_{D25}^{\circ}$  not above  $+4^{\circ}$ ; soluble in every proportion in 90 per cent. alcohol<sup>2)</sup>.

<sup>1)</sup> For the lower limit of value, 1,063 is more suitable (comp. table).

<sup>2)</sup> Not every oil answers this requirement. We have again recently found in one of our own distillates, that 1 to 2 vol. 90 per cent. alcohol are required to dissolve 1 vol. sassafras oil; this observation agrees with those repeatedly made with good commercial oils. Comp. also the present Report p. 61.

**Savin Oil** (*Oleum sabinae*). Colourless or yellowish;  $d_{25}^{\circ}$  0,903 to 0,923;  $\alpha_{D25}^{\circ}$   $+40$  to  $+60^{\circ}$ ; soluble in about 0,5 volumes and more 90 per cent. alcohol.

**Spearmint Oil** (*Oleum menthae viridis*). Colourless, yellow, or greenish yellow;  $d_{25}^{\circ}$  0,914 to 0,934;  $\alpha_{D25}^{\circ}$   $-35$  to  $-48^{\circ}$ ; with an equal volume 80 per cent. alcohol it forms a clear solution which becomes cloudy when further diluted.

**Sweet Orange Oil** (*Oleum aurantii corticis*). Faintly yellow<sup>1)</sup>;  $d_{25}^{\circ}$  0,842 to 0,846;  $\alpha_{D25}^{\circ}$  not below  $+95^{\circ}$ <sup>2)</sup>.

<sup>1)</sup> The colour of orange oil is yellow to yellow-brown.

<sup>2)</sup> Calculated for  $20^{\circ}$ , the rotation is  $+96^{\circ}$ ; we have observed as lowest value at  $20^{\circ}$   $+95^{\circ}30'$ .

**Thyme Oil** (*Oleum thymi*). Colourless<sup>1)</sup>;  $d_{25^{\circ}}$  0,900 to 0,930<sup>2)</sup>; feeble lævorotation,  $\alpha_{D25^{\circ}}$  not above  $-3^{\circ}$ <sup>3)</sup>; phenol-content at least 20 per cent. by volume; soluble in 0,5 vol. alcohol and in 1 to 2 vol. 80 per cent. alcohol.

<sup>1)</sup> The rectified oils also frequently acquire again the red-brown colour of the crude oil.

<sup>2)</sup> 0,900 is too high as lowest limit of value, and this should be 0,894 (comp. table).

<sup>3)</sup> We have also repeatedly observed oils with a feeble dextrorotation; further, the rotation is sometimes a little higher than indicated in the Pharmacopœia. In most cases, the optical behaviour of the oil can only be determined approximately on account of the dark colour.

**Thymol.** Large colourless, transparent rhombic prisms;  $d_{25^{\circ}}$  1,030; melting point 50 to 51°; the alcoholic solution is optically inactive.

**Turpentine Oil** (*Oleum terebinthinæ*). Colourless;  $d_{25^{\circ}}$  0,860 to 0,870<sup>1)</sup>; on distillation the bulk should pass over between 155 and 162°; soluble in 3 vol. alcohol.

<sup>1)</sup> It would be more correct to fix 0,858 as the lowest limit of value (comp. table).

**Turpentine Oil, rectified** (*Oleum terebinthinæ rectificatum*). Colourless;  $d_{25^{\circ}}$  0,860 to 0,865<sup>1)</sup>,

<sup>1)</sup> The lower limit applies to a temperature of 15°; for 25° it is 0,853 (comp. table).

**Vanillin.** Fine, white, crystalline needles; soluble in about 100 parts water of 25°, and in 15 parts of 80°; readily soluble in alcohol; melting point 80 to 81°.

### Wintergreen Oil:

a) **from Betula lenta L.** (*Oleum betulæ*).  $\alpha_D \pm 0^{\circ}$ ; for the rest, the same properties as *Oleum gaultheriæ*.

b) **from Gaultheria procumbens L.** (*Oleum gaultheriæ*). Colourless or almost colourless<sup>1)</sup>;  $d_{25^{\circ}}$  1,172 to 1,180; feeble lævorotation,  $\alpha_{D25^{\circ}}$  up to  $-1^{\circ}$ ; boiling point 218 to 221°.

<sup>1)</sup> The oils are frequently of a reddish colour, owing to traces of iron.

c) **Artificial Wintergreen Oil** (*Methylis salicylas*). Colourless;  $d_{25^{\circ}}$  1,180 to 1,185<sup>1)</sup>;  $\alpha_D \pm 0^{\circ}$ ; boiling point 219 to 221°; soluble in every proportion in alcohol.

<sup>1)</sup> The lower limit is given too high; it should be 1,177 (comp. table).

## Austrian Pharmacopœia.

(Pharmacopœia Austriaca ed. VIII).

Owing to the many incorrect statements regarding essential oils contained in the seventh Edition of the Austrian Pharmacopœia, the eighth Edition just issued is all the more welcome, as the defects

mentioned above have been put right in almost every case, and the requirements specified may, with a few exceptions which still stand in need of correction, be characterised as answering the purpose and up to date. Following the example of other Pharmacopœias, the editors of the Austrian have also endeavoured to replace essential oils wherever possible by their active constituents, as for instance anise oil by anethol, clove oil by eugenol, etc. There has further been added cajeput oil, whilst bergamot oil is now no longer included.

Where "parts" are mentioned, they are parts by weight.

The alcohols coming under consideration are the following:

- a) Spiritus (Spiritus vini concentratus) with 90 to 91,2 per cent. by volume, and
- b) Spiritus dilutus (Spiritus vini dilutus) with 68 to 69 per cent. by volume.

**Anethol** (*Anetholum*). Prepared from anise oil<sup>1)</sup>. White crystalline mass;  $d_{0,984}$  to  $0,986$ <sup>2)</sup>; melting point  $20$  to  $21^{\circ}$ <sup>3)</sup>; boiling point  $232$  to  $234^{\circ}$ ; soluble in 2 parts Spiritus<sup>4)</sup>; volatile when heat is applied, without leaving any (or only a small) residue.

<sup>1)</sup> It is no doubt generally known that fennel oil and star-anise oil are also crude materials for anethol. The anethol is of course the same in every case.

<sup>2)</sup> The specific gravity is for  $25^{\circ}$ .

<sup>3)</sup> The melting point of pure anethol lies between  $22$  and  $23^{\circ}$ , the solidifying point between  $21$  and  $22^{\circ}$ .

<sup>4)</sup> 2 to 3 volumes alcohol of 90 per cent. by vol. are required to dissolve 1 vol. anethol.

**Cajeput Oil** (*Oleum cajuputi*). Green;  $d_{15^{\circ}}$   $0,920$ <sup>1)</sup> to  $0,930$ ; very readily soluble in Spiritus.

<sup>1)</sup> It would be more correct to take  $0,919$  as the lower limit of value.

**Carvone** (*Carvonum*). Colourless or yellowish;  $d_{15^{\circ}}$   $0,960$  to  $0,964$ <sup>1)</sup>; boiling point  $229$  to  $230^{\circ}$ ; soluble in 2 parts spir. dil.

<sup>1)</sup> The specific gravity of pure carvone lies between  $0,963$  and  $0,966$ .

**Cinnamic Aldehyde** (*Cinnamalum*). Obtained from cassia oil<sup>1)</sup>; yellow;  $d_{15^{\circ}}$   $1,054$  to  $1,056$ <sup>2)</sup>; soluble in every proportion in Spiritus; if 2 cc. cinnamic aldehyde are mixed with the same quantity sodium bisulphite solution ( $30\%$ ), and heated on a waterbath, a solid mass should be formed, which must dissolve completely when heated further and when 22 cc. bisulphite solution are gradually added; test for nitric acid; ferric chloride reaction.

<sup>1)</sup> The commercial cinnamic aldehyde is usually produced synthetically, as the production from cassia oil would be too expensive.

<sup>2)</sup> The specific gravity is also some times higher; we have observed in our own preparations up to  $1,058$ .

**Eugenol** (*Eugenolum*). Colourless or yellowish, in course of time becoming brownish;  $d_{15^{\circ}}$   $1,072$  to  $1,074$ <sup>1)</sup>; boiling point  $252$  to  $254^{\circ}$ <sup>2)</sup>;

dissolves with difficulty in water, readily in Spiritus, ether, and glacial acetic acid. When 1 gm. eugenol is mixed with 26 cc. water and 4 cc. soda liquor (15%), a clear solution should be formed, which becomes cloudy on exposure to the air. Identity-reaction with ferric chloride and test for phenol.

<sup>1)</sup> The absolutely water-free preparation distilled *in vacuo*, is often also somewhat lighter; with our own distillates we have observed down to 1,0713. Comp. also Report April 1902, 72.

<sup>2)</sup> It is difficult to determine the boiling point exactly as partial decomposition occurs in boiling.

**Fennel Oil** (*Oleum fœniculi*). Colourless or faintly yellow;  $d_{15^{\circ}}$  0,965 to 0,975; soluble in an equal vol. Spiritus; when cooled down to a few degrees below  $0^{\circ}$ , fennel oil must separate off anethol crystals which melt again at  $+5^{\circ}$ <sup>1)</sup>.

<sup>1)</sup> It would have been better to have substituted for the above, the requirement of a definite solidifying point which should not lie below  $+4^{\circ}$ . But it should be taken into consideration that the solidification may have to be started by inoculation with a small crystal of anethol, as under certain conditions it is possible to cool fennel oil strongly without causing solidification.

**Oil of Juniper berries** (*Oleum juniperi*). Colourless or greenish yellow;  $d_{15^{\circ}}$  0,865 to 0,880<sup>1)</sup>; dissolves with difficulty in Spiritus<sup>2)</sup>.

<sup>1)</sup> The limits should here be wider: 0,860 to 0,885.

<sup>2)</sup> Only the freshly distilled oils dissolve in 5 to 10 vol. 90 per cent. alcohol; in the course of time the solubility diminishes very much.

**Lavender Oil** (*Oleum lavandulæ*). Colourless or faintly yellow;  $d_{15^{\circ}}$  0,885 to 0,895; very readily soluble in Spiritus.

**Lemon Oil** (*Oleum citri*). Bright yellow;  $d_{15^{\circ}}$  0,858 to 0,861; soluble in 5 parts Spiritus<sup>1)</sup>.

<sup>1)</sup> Owing to its content of slimy and vegetable wax-like constituents, lemon oil forms mostly only a cloudy solution with 90 per cent. alcohol.

**Mace Oil** (*Oleum macidis*). Colourless or yellowish, becomes in course of time brownish;  $d_{15^{\circ}}$  0,890 to 0,930; forms a clear solution with 3 parts Spiritus.

**Menthol** (*Mentholum*). Prismatic or needle-shaped colourless crystals; melting point  $42$  to  $43^{\circ}$ ; dissolves with difficulty in water, readily in Spiritus, ether, and chloroform; 10 gr. menthol must be completely volatile at the temperature of the water-bath, without discolouring. If menthol is added to a mixture of 1 cc. glacial acetic acid, 3 drops concentrated sulphuric acid, and 1 drop nitric acid no coloration may occur.

**Mustard Oil** (*Oleum sinapis æthereum*). Colourless or yellow<sup>1)</sup>;  $d_{15^{\circ}}$  1,016 to 1,025; boiling point  $148$  to  $152^{\circ}$ ; readily soluble in Spiritus and ether, little in water; the aqueous solution decomposes rapidly. Sulphuric acid reaction, and test with ferric chloride.

<sup>1)</sup> In the course of time mustard oil acquires a reddish brown colour.

**Neroli Oil** (*Oleum aurantii florum*). When freshly distilled colourless<sup>1)</sup> or faintly yellow, becoming darker in the course of time, and finally brown-yellow;  $d_{15^{\circ}}$  0,870 to 0,880; dissolves very readily in spiritus; the spirituous solution shows a bluish fluorescence.

<sup>1)</sup> The fresh distillate also is never colourless, but always yellowish.

**Peppermint Oil** (*Oleum menthae piperitæ*). Colourless, yellowish or greenish-yellow;  $d_{15^{\circ}}$  0,900 to 0,910; forms a clear solution with 4 to 5 parts spir. dil. A mixture of 5 drops peppermint oil and 1 cc. glacial acetic acid must after a few hours show a blue coloration; the blue colour occurs more rapidly if to 2 cc. oil and 1 cc. glacial acetic acid, 1 drop nitric acid is added<sup>1)</sup>.

<sup>1)</sup> Judging from the specific gravity, only English oil is admitted. For this reason it is all the more incomprehensible why the colour-reaction, which applies specially to American oil, has been included, which is of no importance whatever for judging the value of peppermint oil; even with the best Mitcham oil the reaction does not by any means occur in every case, a fact of which we have convinced ourselves repeatedly. In the presence of nitric acid a more or less powerful blue coloration occurs in every case.

**Oil of Pinus pumilio** (*Oleum pini pumilionis*). Colourless;  $d_{15^{\circ}}$  0,865 to 0,875; commences to boil at  $165^{\circ}$ ; completely soluble in Spiritus<sup>1)</sup>.

<sup>1)</sup> For dissolving 1 vol. oil, 5 to 8 vol. 90 per cent. alcohol are required; sometimes a clear solution is not formed at all.

**Rose Oil** (*Oleum rosae*). Yellowish;  $d_{20^{\circ}}$  0,855 to 0,870; solidifying point  $15$  to  $22^{\circ}$ ; soluble in about 30 parts Spiritus with slight opalescence<sup>1)</sup>.

<sup>1)</sup> Owing to its content of difficultly soluble paraffins, rose oil always forms only cloudy solutions with 90 per cent. alcohol, from which the paraffins gradually separate out.

**Rosemary Oil** (*Oleum rosmarini*). Colourless or yellowish;  $d_{15^{\circ}}$  0,900 to 0,920; very readily soluble in Spiritus.

**Sandalwood Oil, East Indian** (*Oleum santali*). Bright yellow;  $d_{15^{\circ}}$  0,975 to 0,980<sup>1)</sup>; boiling point  $275$  to  $305^{\circ}$ ; acid reaction; saponification number 5 to 15<sup>2)</sup>; at  $20$  to  $30^{\circ}$  forms a clear solution with 5 parts spir. dil.

<sup>1)</sup> The upper limit is given too low and should be: 0,985.

<sup>2)</sup> The saponification numbers of sandal oil lie between 5 and 20.

**Sweet Orange Oil** (*Oleum aurantii pericarpium*).  $d_{15^{\circ}}$  0,848 to 0,852; readily soluble in Spiritus<sup>1)</sup>; in the course of time crystalline separations occur which are soluble in Spiritus<sup>2)</sup>.

<sup>1)</sup> For dissolving 1 vol. oil, 8 to 10 vol. 90 per cent. alcohol are required, but the solution is never perfectly clear on account of the wax-like constituents always present in the oil.

<sup>2)</sup> The separations which are chiefly of the character of vegetable wax, dissolve with some difficulty in Spiritus.

**Thymol** (*Thymolum*). Colourless crystals in the form of tablets; melting point 50 to 51°; soluble in about 1100 parts water; readily soluble in Spiritus, ether, chloroform, and also in soda liquor; solid thymol sinks in water, but when melted it floats on the surface; when evaporated on a water bath, 10 gr. thymol must leave no weighable residue. Colour reactions.

**Turpentine Oil** (*Oleum terebinthinæ*). Colourless or faintly yellow;  $d_{15^{\circ}}$  0,865 to 0,870<sup>1)</sup>; commences to boil at 160°; forms a clear solution with about 8 parts Spiritus; it absorbs oxygen from the air, and then becomes more viscid.

<sup>1)</sup> The crude oil is frequently heavier, up to 0,877.

<sup>2)</sup> Turpentine oil commences to boil at about 155°.

**Turpentine Oil, rectified** (*Oleum terebinthinæ rectificatum*). Colourless;  $d_{15^{\circ}}$  0,860 to 0,870; boiling point 155 to 162°; soluble in about 7 parts Spiritus; the solution should not change litmus paper moistened with water.

**Valerian Oil** (*Oleum valerianæ*). Yellow-green or brown-yellow; at first mobile, becoming more viscid in course of time;  $d_{15^{\circ}}$  0,93 to 0,96; acid reaction; dissolves with difficulty in water, very readily in Spiritus.

## Spanish Pharmacopœia.

(Farmacopea oficial española, séptima edición 1905.)

On the new seventh edition of the Spanish Pharmacopœia, it is unfortunately not possible, so far as concerns the articles which interest us, to pronounce as favourable an opinion as on the other Pharmacopœias discussed in these pages. At first sight it no doubt appears as if a modern spirit pervaded throughout the directions for testing, as the Pharmacopœia even specifies definite demands for the optical rotatory power of the oils; but on closer examination the exact opposite is found to be the case. For example, the rotations given are partly entirely incorrect, and many of the other details are so antiquated that one involuntarily receives the impression that the knowledge of the progress made in the examination of essential oils during the last 20 years, has not yet penetrated to Spain. This fact makes it appear all the more desirable to discuss here the individual oils.

In vain we have looked for information as to the temperature to which the specific gravities mentioned for the various oils apply.

As for other liquids they have all been taken at 15°, it may be assumed that in the case of essential oils that temperature has also been taken as a basis. For this reason we have in the following pages judged the specific gravities in every case accordingly.

Of alcohols, there are admitted an alcohol of  $95^{\circ}$  (95 per cent. by volume), and one of  $60^{\circ}$  (60 per cent. by volume).

**Anise Oil** (*Esencia de anís*). Colourless;  $d_{15^{\circ}}$  0,984 to 0,986<sup>1)</sup>; solidifies at  $+10^{\circ}$  into a white crystalline mass<sup>2)</sup>; soluble in alcohol in every proportion; the alcoholic solution must not redden litmus paper, and its colour must not change when ferric chloride is added.

<sup>1)</sup> As solidification sometimes occurs already spontaneously at  $15^{\circ}$ , it is advisable to determine the specific gravity at  $20^{\circ}$ ; the limits of value lie between 0,980 and 0,990, those given above are incorrect.

<sup>2)</sup> Solidification has frequently to be started by inoculation with a small crystal of solid anethol, as anise oil can under certain conditions be cooled very much without solidifying. The solidification point of good oils lies above  $+17^{\circ}$ ; for the determination, comp. Gildemeister and Hoffmann, "The Volatile Oils", p. 187.

**Bergamot Oil** (*Esencia de bergamota*). Obtained from the peel of the bergamot by expression or by distillation with water vapour<sup>1)</sup>; yellowish-green or green<sup>2)</sup>;  $d_{15^{\circ}}$  0,86 to 0,88<sup>3)</sup>;  $\alpha_D$  to the right; soluble in one half volume 85 per cent. alcohol, and in potash liquor<sup>4)</sup>; 4 vol. oil form a clear solution with 1 vol. carbon disulphide, which becomes cloudy when more carbon disulphide is added.

<sup>1)</sup> The oil obtained in the usual manner by distillation with water vapour is inferior. Comp. Gildemeister and Hoffmann, "The Volatile Oils", p. 474.

<sup>2)</sup> Bergamot oil has also frequently, especially in the fresh state, a brown or honey colour. Distilled bergamot oil is colourless.

<sup>3)</sup> The specific gravity of the oil obtained by expression lies between 0,881 and 0,886; the distilled oils are somewhat lighter (0,865 to 0,880).

<sup>4)</sup> In ordinary aqueous potash liquor bergamot oil is not soluble.

**Bitter Almond Oil** (*Esencia de almendras amargas*). When freshly distilled, colourless, subsequently yellowish;  $d_{15^{\circ}}$  1,043<sup>1)</sup>;  $\alpha_D \pm 0^{\circ}$ <sup>2)</sup>; soluble in 30 parts water<sup>3)</sup>, in every proportion in alcohol and ether. It should not react<sup>4)</sup> violently with iodine which dissolves slowly in it; when mixed with sulphuric acid it should acquire a brown colour which disappears again almost completely when alcohol is added. If a mixture of 1 part oil, 8 parts alcohol and 1 part potash is heated until  $2/3$  of the alcohol have evaporated, no crystalline residue should remain behind, and the liquid should have a yellowish-brown colour.

<sup>1)</sup> The specific gravity lies at  $15^{\circ}$  between 1,045 and 1,070.

<sup>2)</sup> Sometimes a very slight optical activity is observed.

<sup>3)</sup> The solution is not complete even if more water is added; the bulk of the oil separates out again when the mixture is left standing.

<sup>4)</sup> Such reactions are of no importance whatever for judging essential oils; for this reason they are not mentioned again in the following pages. The same applies to tests of a similar character, as for example colour-reactions.

**Cajeput Oil** (*Esencia de cayeput*). Colourless, yellowish-green, or emerald green;  $d_{15^{\circ}}$  0,91 to 0,95<sup>1)</sup>;  $\alpha_D \pm 0^{\circ}$ <sup>2)</sup>; neutral; readily soluble in alcohol and acetic acid and alcohol, but not in carbon disulphide<sup>3)</sup>.

<sup>1)</sup> The limits of value might have been drawn narrower;  $d_{15^{\circ}}$  0,919 to 0,930.

<sup>2)</sup> Cajeput oil is slightly lævorotatory,  $\alpha_D$  to  $-2^{\circ}40'$ .

<sup>3)</sup> All essential oils dissolve in carbon disulphide; any cloudiness occurring thereby must be attributed to the small content of water due to the manner of production of the oils.

**Cinnamon Oil, Ceylon** (*Esencia de canela*). Golden yellow, in course of time reddish;  $d_{15^{\circ}}$  1,004 to 1,006<sup>1)</sup>;  $\alpha_D$  slightly to the left; nitric acid test, ferric chloride reaction.

<sup>1)</sup> Ceylon cinnamon oil has at  $15^{\circ}$  a specific gravity of 1,023 to 1,040.

**Citron Oil**<sup>1)</sup> (*Esencia de cidra*). Obtained from the peel of the cedro or citron by expression or distillation with water vapour<sup>2)</sup>; colourless<sup>3)</sup> or yellowish;  $d_{15^{\circ}}$  0,852 to 0,856<sup>4)</sup>;  $\alpha_D$  to the right; soluble in every proportion in carbon disulphide and in 95 per cent. alcohol; with weaker alcohol cloudy solutions are formed<sup>5)</sup>.

<sup>1)</sup> As citron oil is not a commercial article, its admission to the Pharmacopœia is difficult to explain.

<sup>2)</sup> The oils obtained by distillation are inferior.

<sup>3)</sup> Only the distilled oils are colourless.

<sup>4)</sup> With reference to the specific gravity of citron oils, comp. our Reports April 1902, 30, October 1902, 35, and April 1903, 34.

<sup>5)</sup> The solutions in carbon disulphide are usually slightly turbid owing to the content of water in the oil; of 95 per cent. alcohol about 0,5 to 1 vol. are required to form a clear solution.

**Clove Oil** (*Esencia de clavo*). Freshly distilled colourless, subsequently yellowish, reddish, or brown;  $d_{15^{\circ}}$  1,04 to 1,06<sup>1)</sup>;  $\alpha_D$  to the left; acid reaction; ferric chloride must not cause blue coloration.

<sup>1)</sup> The specific gravity is occasionally also higher, up to 1,07 ( $15^{\circ}$ ).

**Eucalyptol** (*Eucaliptol*). Colourless;  $d_{0^{\circ}}$  0,940<sup>1)</sup>; at a low temperature solidifying into a crystalline mass, which melts again at  $1^{\circ}$ <sup>2)</sup>; boils at  $174^{\circ}$ <sup>3)</sup>; soluble in every proportion in absolute alcohol, in carbon disulphide and in glacial acetic acid.

<sup>1)</sup> The specific gravity of eucalyptol at  $15^{\circ}$  is 0,928 to 0,930.

<sup>2)</sup> The melting point does not lie at  $+1^{\circ}$ , but at  $-1^{\circ}$ .

<sup>3)</sup> Eucalyptol boils at 760 mm between  $176$  and  $177^{\circ}$ .

**Eucalyptus Oil** (*Esencia de eucalipto*). Colourless or yellowish;  $d_{15^{\circ}}$  0,90 to 0,92<sup>1)</sup>;  $\alpha_D$  to the right; neutral; soluble in an equal part by weight of alcohol.

<sup>1)</sup> More correct is an upper limit of 0,93.

**Lavender Oil** (*Esencia de espliego*). Colourless, yellowish or greenish-yellow;  $d_{15^{\circ}}$  0,87 to 0,94<sup>1)</sup>;  $\alpha_D$  to the left; acid reaction; soluble in every proportion in 85 per cent. alcohol.

The oil of *Lavandula spica* D. C. is dextrorotatory.

<sup>1)</sup> The limits of value are here so far apart, that most adulterated oils would also answer the requirements; with pure oil, the specific gravity fluctuates between 0,882 and 0,895 ( $15^{\circ}$ ).

**Lemon Oil** (*Esencia de limón*). Obtained from the peel of the lemon by expression or distillation by water vapour<sup>1)</sup>. The oil obtained

by expression is yellowish and turbid<sup>2)</sup>, separating off stearoptene<sup>3)</sup> at  $-20^{\circ}$ , possessing a very pleasant odour; the distilled oil is colourless and has a less pleasant odour;  $d_{15^{\circ}}$  below 1;  $\alpha_D$  to the right<sup>4)</sup>; soluble in ether and 95 per cent. alcohol, forms only cloudy solutions with 85 per cent. alcohol.

<sup>1)</sup> Distillation of the oil is quite irrational, as such oils rapidly deteriorate and then acquire an unpleasant pungent odour.

<sup>2)</sup> At ordinary temperature lemon oil is mostly clear; a possible turbidity is caused by slimy or vegetable wax-like constituents.

<sup>3)</sup> The separation called "stearoptene" consists of substances of the character of vegetable wax.

<sup>4)</sup> More precise data would here be very much to the point. The specific gravity of good lemon oil obtained by expression lies between 0,857 and 0,861 ( $15^{\circ}$ ) and the rotation between  $+58$  and  $+65^{\circ}$  (at  $20^{\circ}$  C).

<sup>5)</sup> Of 95 per cent. alcohol about 1 vol. is required to form a solution.

**Menthol** (*Mentol*). Colourless needles;  $d_{15^{\circ}}$  0,89;  $\alpha_D$  to the left; melting point  $42^{\circ}$ <sup>1)</sup>; boiling point  $208^{\circ}$ <sup>2)</sup>; scarcely soluble in water, readily soluble in alcohol, ether, chloroform, and fatty oils; volatilises without residue.

<sup>1)</sup> Melting point  $42$  to  $43^{\circ}$ .

<sup>2)</sup> Boiling point  $212^{\circ}$  (760 mm).

**Mustard Oil** (*Esencia de mostaza negra*). Colourless or yellowish; when exposed to the air, decomposition occurs with red or brown coloration;  $d_{15^{\circ}}$  1,018<sup>1)</sup>; boiling point about  $148^{\circ}$ <sup>2)</sup>; readily soluble in alcohol, ether, and chloroform; should not contain any fatty oil; a solution of 1 part mustard oil in 5 parts alcohol must not be coloured red or blue by ferric chloride.

<sup>1)</sup> The specific gravity of mustard oil at  $15^{\circ}$  fluctuates between 1,014 and 1,025.

<sup>2)</sup> On distillation the bulk of mustard oil passes over between  $148$  and  $153^{\circ}$ .

**Neroli Oil** (*Esencia de azahar*). Colourless<sup>1)</sup>, in course of time yellowish;  $d_{15^{\circ}}$  0,85 to 0,90<sup>2)</sup>;  $\alpha_D$  to the right; neutral<sup>3)</sup>; when at rest, separation of a white crystalline mass, which dissolves with difficulty in alcohol. Taste aromatic, not bitter<sup>4)</sup>.

<sup>1)</sup> Neroli oil is never colourless, but right from the first yellowish; in course of time it becomes reddish-brown.

<sup>2)</sup> The specific gravity lies between 0,870 and 0,880.

<sup>3)</sup> Oils containing ester show almost always a minute content of free acid.

<sup>4)</sup> The after-taste is somewhat bitter.

**Peppermint Oil** (*Esencia de menta piperita*). Colourless or yellowish green;  $d_{15^{\circ}}$  0,89 to 0,92;  $\alpha_D$  to the left; acid reaction; readily soluble in alcohol.

**Rosemary Oil** (*Esencia de romero*). Colourless or yellowish;  $d_{15^{\circ}}$  0,88 to 0,91<sup>1)</sup>;  $\alpha_D$  to the left<sup>2)</sup>; neutral reaction; soluble in every proportion in 85 per cent. alcohol<sup>3)</sup>.

<sup>1)</sup> More correct would be 0,89 to 0,92.

<sup>2)</sup> Pure rosemary oil is dextrorotatory; lævorotation would point to adulteration with French oil of turpentine.

<sup>3)</sup> Rosemary oil is also frequently not soluble in every proportion in 85 per cent. alcohol.

**Sandalwood Oil, East Indian** (*Esencia de sándalo*). Bright yellow;  $d_{15^{\circ}}$  0,970 to 0,985;  $\alpha_D$  to the left; neutral or weak acid reaction; readily soluble in alcohol.

**Sassafras Oil** (*Esencia de sasafrás*). Freshly distilled colourless or bright-yellow; subsequently yellow to reddish;  $d_{15^{\circ}}$  above 1;  $\alpha_D$  to the right; neutral reaction; soluble in 4 to 5 parts 85 per cent. alcohol.

**Sweet orange Oil** (*Esencia de naranja*). Obtained from the peel of the fruit of *Citrus aurantium* Risso by expression or distillation by water vapour<sup>1)</sup>; colourless or bright yellow<sup>2)</sup>;  $d_{15^{\circ}}$ , according to the method of production, 0,835 to 0,844<sup>3)</sup>;  $\alpha_D + 82^{\circ}$ <sup>4)</sup>; readily soluble in absolute alcohol, ether, and fatty oils.

<sup>1)</sup> It is not expedient to produce the oils by ordinary distillation with water vapour, as distilled oils readily deteriorate and then acquire a stale, unpleasant odour.

<sup>2)</sup> Only the distilled oils are colourless, the colour of expressed oil is yellow to yellow-brown.

<sup>3)</sup> The specific gravity of sweet orange oil lies at  $15^{\circ}$  between 0,849 and 0,853; distilled oils are somewhat lighter.

<sup>4)</sup> Commercial oil at  $20^{\circ}$  rotates between  $+95^{\circ} 30'$  and  $+98^{\circ}$ ; to what kind of oil the rotation mentioned above applies is incomprehensible.

**Terpin hydrate** (*Terpina*)<sup>1)</sup>. Colourless and odourless prisms which melt at  $116^{\circ}$  with loss of water; soluble in 250 parts cold and 32 parts boiling water, readily soluble in alcohol and ether, further in glycerin and in oil of turpentine; when boiled with greatly diluted sulphuric acid, terpineol is formed; it must not have a turpentine odour, and its aqueous solution must not redden litmus paper; burns with a highly luminous flame without leaving any residue.

<sup>1)</sup> The Pharmacopœia mentions *terpina*, but means terpin hydrate. As terpin and terpin hydrate are two different compounds, a more exact description would have been necessary.

**Terpinol**<sup>1)</sup> Colourless or faint yellow;  $d_{15^{\circ}}$  0,852;  $\alpha_D \pm 0^{\circ}$ ; boiling point  $168^{\circ}$ ; dissolves with great difficulty in water; soluble in alcohol and ether. By the action of nitric acid it is converted into terpin hydrate.

<sup>1)</sup> A compound terpinol does not exist. What used to be called terpinol is, according to Wallach's researches, a mixture of terpineol and terpenes. Comp. Liebig's Annalen 230 (1885), 271.

**Thyme Oil** (*Esencia de tomillo*). Colourless or yellowish<sup>1)</sup>;  $d_{15^{\circ}}$  0,89<sup>2)</sup>;  $\alpha_D$  to the left; neutral reaction; soluble in an equal volume 85 per cent. alcohol.

<sup>1)</sup> Thyme oil is usually somewhat dark in colour, and the rectified oils frequently acquire again in a short time the red-brown colour of the crude oil.

<sup>2)</sup> This value must be considered as the lowest limit of the specific gravity.

**Thymol** (*Timol*). Large crystals of the melting point  $44^{\circ 1)$  and boiling point  $230^{\circ}$ . Very little soluble in water (about 1:340), readily soluble in alcohol, ether, and glacial acetic acid, in fatty oils and the alkalies. The aqueous solution must be neutral, and not become discolored when ferric chloride is added; when heated on a water bath, thymol should leave no residue.

<sup>1)</sup> Thymol melts at 50 to  $51^{\circ}$ .

**Turpentine Oil** (*Esencia de trementina*). Colourless;  $d_{15^{\circ}}$  0,85 to 0,87<sup>1)</sup>;  $\alpha_D$ , according to origin, to the left or right; soluble in ether, chloroform and absolute alcohol in every proportion, also in 4 vol. 90 per cent. alcohol, and in 12 vol. 81 per cent. alcohol<sup>2)</sup>.

<sup>1)</sup> The specific gravity is also frequently higher, up to 0,877.

<sup>2)</sup> Turpentine oil dissolves in 5 to 7 vol. 90 per cent. alcohol, and in 12 to 14 vol. 81 per cent. alcohol.

## Chemical Preparations and Drugs.

**Benzaldehyde.** We have convinced ourselves that the products described in commerce as "free from chlorine" do not always deserve this designation; we would recommend purchasers to pay special attention to this point, and send us samples for testing. The removal of the last traces of chlorine is not such a simple matter, but is necessary if the product is to be described as absolutely free from chlorine.

**Benzyl acetate.** This preparation, which within the last few years has come greatly in favour on account of its pleasant fruity odour, is also supplied by us absolutely free from chlorine, and, as we manufacture it on a large scale, we can offer it at a very advantageous price.

**Benzyl benzoate,** a constituent of Peru balsam, is also well introduced, and is used chiefly as a fixing agent for highly volatile perfumes; it is specially adapted for this purpose on account of its balsamic odour and great stability. It is also recommended as a solvent for artificial musk.

**Citral.** Improved manufacturing processes and a production on a constantly growing scale enable us to meet all competition in this article. The use of it is growing more and more, since the prejudices have been overcome with which this body was received when we discovered it some 18 years ago, and introduced it to the consumers.

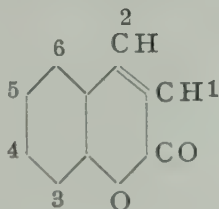
**Coumarin.** A work by Ph. Chuit<sup>1)</sup> and Fr. Boelsing supplies a valuable contribution towards the knowledge of the coumarins alkylised in the benzene nucleus, of which up to the present little was known. In order to arrive at 3-methyl coumarin<sup>2)</sup>, they condensed, according to Knœvenagels<sup>3)</sup> method, malonic acid with o-homosalicyclic aldehyde, with application of aniline hydrochloride. The resulting product of condensation, 3-methyl coumarin carboxylic acid, forms white needles of the melting point 142 to 143°. On distillation at ordinary pressure it yields 3-methyl coumarin of the boiling point 178° (20 mm. press.); melting point 109 to 110°. This body has a faint odour of coumarin. 3-Methyl 1-aceto coumarin forms odourless, faintly yellow crystals of the melting point 125,8 to 126,2°.

Its phenyl hydrazone melts at 168 to 169°, its semicarbazone at 224 to 225°. 3-Methyl coumarin carboxylic acid ester is formed during the condensation of the above aldehyde with malonic acid ester, with application of piperidine as condensing agent; odourless, brilliant crystals of the melting point 81°.

The above-mentioned chemists proceeded in an entirely analogous manner to produce the remaining homocoumarins and their derivatives. Contrary to H. Schmidt<sup>4)</sup>, who obtained by Perkin's method from m-homosalicyclic aldehyde, by heating with acetic acid anhydride and sodium acetate to 220°, a methyl coumarin melting at 90°, Chuit and Boelsing arrived at two different methylated coumarins. They proved at the same time that Schmidt's preparation was a mixture of two homocoumarins, whose formation could be thus explained, that the m-homosalicyclic aldehyde used for the condensation was a mixture of two isomerides, methyl phenol-3-methylal-4 and methyl phenol-3-methylal-2. The first aldehyde of the melting point 59° yields on condensation with malonic acid, 4-methyl coumarin-1-carboxylic acid of the melting point 198,8 to 199,8°. The 4-methyl coumarin which can be obtained from it, melts at 125,8° to 126,4°, and has a fairly strong odour of coumarin. The other m-homosalicyclic aldehyde, methyl phenol-3-methylal-2, of the melting point 31,5°, condenses

<sup>1)</sup> Bull. Soc. Chim. III. **35** (1906), 76.

<sup>2)</sup> The coumarin formula is based on the designation of Simonis and Wenzel (Berl. Berichte **33** [1905], 2327): —



<sup>3)</sup> Berl. Berichte **31** (1898), 2585, 2696.

<sup>4)</sup> Thesis, Rostock 1897.

with malonic acid to 6-methyl coumarin-1-carboxylic acid of the melting point  $162,5$  to  $163^{\circ}$ . The 6-methyl coumarin corresponding to it has the melting point  $65$  to  $65,8^{\circ}$ . It possesses only a feeble coumarin odour. The two methyl coumarins produced by the authors according to Perkin's method, show the same melting point, which disproves Schmidt's observation. The 4-methyl coumarin-1-carboxylic acid ester which can be derived from the methyl phenol-3-methylal-4, and which is obtained in a manner analogous to the method described above, forms brilliant leaflets, which melt between  $101,5$  and  $102,5^{\circ}$ . 4-methyl-1-aceto coumarin of the melting point  $156$  to  $157^{\circ}$  yields an oxime which melts at  $224^{\circ}$ . The other carboxylic acid ester which is derived from methyl phenol-3-methylal-2, forms brilliant needles of the melting point  $122$  to  $122,5^{\circ}$ . 6-methyl-1-aceto coumarin shows the melting point  $115^{\circ}$ , its oxime that of  $214^{\circ}$ .

The condensation of p-homosalicyclic aldehyde (methyl phenol-4-methylal-3) with malonic acid leads to 5-methyl coumarin carboxylic acid of the melting point  $166,8^{\circ}$ . Its ester forms odourless, transparent tablets of the melting point  $103$  to  $104^{\circ}$ . 5-methyl coumarin has, of all the homocoumarins described, the most powerful odour, but it differs slightly in the odour from ordinary coumarin. The latter is more penetrating, but not so persistent as the former. In view of the high price of p-homosalicyclic aldehyde, or p-cresol, 5-methyl coumarin appears hardly capable of competing with ordinary coumarin. 5-methyl coumarin boils at 14 mm. pressure at  $174^{\circ}$ , and melts at  $74,6$  to  $75^{\circ}$ . Its acetyl derivative of the melting point  $128$  to  $128,4^{\circ}$ , is obtained in a manner analogous to the former; semicarbazone melting point  $211^{\circ}$ ; oxime melting point  $219^{\circ}$ ; phenyl hydrazone melting point  $193$  to  $194^{\circ}$ .

The same authors<sup>1)</sup> have subsequently published the results of their examination of the two above-mentioned m-homosalicyclic aldehydes. A separation of these bodies, produced, according to the method of Tiemann and Schotten<sup>2)</sup>, by the action of chloroform on m-cresol, can be effected by repeated treatment of the aldehyde mixture with small quantities of dilute soda liquor, when only the aldehyde of the melting point  $59^{\circ}$  is dissolved. Another method of separation is based on the different solubilities of their calcium salts in hot water. The calcium salt of methyl phenol-3-methylal-2 of the melting point  $32^{\circ}$  dissolves with difficulty, and is precipitated in the form of yellowish crystals, when a hot dilute solution of calcium chloride is added to the hot soda liquor solution of the aldehyde mixture, whilst the salt of the methyl phenol-3-methylal-4 melting at  $59^{\circ}$  remains in solution in the mother-liquor and only separates out on cooling.

<sup>1)</sup> Bull. Soc. Chim. III. **35** (1906), 129.

<sup>2)</sup> Berl. Berichte **11** (1878), 773.

The methyl phenol-3-methylal-4 purified from the calcium salt, melts at 59 to 59,8°, and boils at 219 to 221° (726 mm. pressure). It has a very pleasant odour, reminding of that of pure salicylic aldehyde. Melting point of the oxime 108,5 to 109°; melting point of the semicarbazone 254 or 272°; melting point of the phenyl hydrazone 160 to 160,5°. When heated with caustic potash to 220°, it oxidises into m-cresotinic acid ( $\alpha$ -m-homosalicylic acid) of the melting point 176°; its methyl derivative yields with the same reaction also m-cresotinic acid, and on oxidation with potassium permanganate methoxyterephthalic acid of the melting point 277 to 279°. From these results the constitution of the aldehyde is at once apparent. Its isomeride, methylphenol-3-methylal-2 of the melting point 31,4 to 31,9° boils at 728 mm. pressure at 228 to 229,3°. The odour of this body resembles that of salicylic aldehyde. Melting point of the oxime 111 to 112°; melting point of the semicarbazone 214 or 244° respectively; melting point of the phenyl hydrazone 170,2 to 171,4°. Caustic potash converts it a 220° into  $\beta$ -m-homosalicylic acid of the melting point 168 to 169°. Its methyl ether is converted on oxidation with potassium permanganate into 3-methoxy-o-toluylic acid of the melting point 139°.

**Eucalyptol (cineol), crystallising.** We would here again call attention to the fact that we only manufacture the pure body. This has a melting point of — 1°, and is optically inactive. We lay special stress on these properties, as they are characteristic of the pure body, and as products are met with in commerce which are offered as eucalyptol, but which are nothing else than a rectified eucalyptus oil. Such makeshifts can naturally be supplied at a decidedly lower price than our product.

**Geraniol from palmarosa oil.** With the low price of palmarosa oil, this preparation now comes cheaper than the one prepared from citronella oil, and can be supplied in any quantity. It possesses a fine rose-like odour, and deserves to be submitted to a thorough test.

**Heliotropin.** The price of this product has now reached the extreme limit of possibility. In consequence of this the use has increased tenfold during the last few years.

**Linalyl acetate.** This body, as is well known, is the characteristic principal constituent of lavender oil and bergamot oil. It is manufactured by us by chemical process in the pure state, and contains about 80% linalyl acetate; the remainder of about 20% consists of linalool, which is also present in the free state in oil of bergamot.

Linalyl acetate is therefore to be considered as a concentrated terpenless bergamot oil, practically about 2½ times stronger than

ordinary oil of a good quality. Although the price does not at present permit the use on a large scale, it is possible that under favourable circumstances linalyl acetate might come to play the part of a substitute of bergamot oil. If only from this point of view, the manufacture of linalyl acetate must be welcomed.

In the perfumery trade it can be used in every case where the bulk of ordinary bergamot oil in the manufactured product is inconvenient.

A further advantage is its being absolutely colourless.

**Menthol.** With regard to the commercial situation of this preparation, the same applies as what has been said on p. 53 of the present Report on the subject of Japanese oil of peppermint. Here also the bears and bulls are standing face to face, and it is doubtful which of the two will finally carry the day. The result will to a large extent depend upon this, whether the cultivation of peppermint in Japan has actually been restricted as stated, or whether that statement has only the character of a hollow phrase.

It is a fact that the consumption of menthol is still going up, and that the number of medicinal and cosmetic preparations based on menthol is constantly increasing. In view of the probably unique usefulness and popularity of menthol, a decline of the value is in our opinion scarcely to be expected; on the contrary, the present prices should be taken advantage of for laying in an abundant stock for the current year.

This suggestion is fully supported by the statistical figures, for only in the years 1888 and 1889 has the price of purified menthol been lower than now. This article made its first appearance in our lists in March 1881, at 140 marks per kilo, then kept itself for a long time at 100 marks, and subsequently took a pronounced downward course, with periodical upward movements.

Total value of menthol shipments from Japan in the years  
1900 to 1904.

	1900	1901	1902	1903	1904
	Yen	Yen	Yen	Yen	Yen
to British India . .	20875	18807	11698	23020	63955
„ France . . . .	4950	25212	22565	43317	141075
„ Germany . . . .	46391	100040	71045	193729	159496
„ the United Kingdom	62995	9706	90833	155406	229685
„ Hong Kong . . .	13964	163884	127369	219189	156770
„ the United States .	23000	111130	126525	162754	326784
„ other countries . .	326	8273	13684	6987	12973
Totals	172501	437052	463719	804402	1090743

**Safrol.** The advancing prices of camphor oil will in course of time have to be taken into consideration in calculating the price of safrol. For the present we are still working up material bought by us at low prices and for that reason have still refrained from raising our quotations.

**Terpineol.** On the basis of the present prices of oil of turpentine, the quotations of terpineol ought to be raised considerably but for the fact that these unfavourable conditions are counteracted by improvements in the manufacture.

We produce only one quality, which is of the greatest purity and possesses an incomparable fragrance. In spite of the large increase in our plant, we are scarcely able to meet the demand — the best proof, no doubt, of the excellent quality of our product.

We have in our Reports repeatedly warned against attaching too great a value to colour reactions in the terpene chemistry. In spite of this, new ones are recommended again and again, which often already at the outset appear of little value. This, for example, is the case with the reaction mentioned by C. Reichard<sup>1)</sup> for the detection of terpineol in mixtures of perfumes, essential oils, etc. This reaction is accomplished as follows: — In a small porcelain dish are given a few drops of a strong aqueous solution of potassium thiocyanate; this is heated until a slight crust of solid salt separates out at the margin of the liquid, and a small drop of terpineol is then added. If a drop of concentrated sulphuric acid is added to this mixture starting from the edge, there occurs at ordinary temperature immediately an intense coloration which usually appears to be brown-red, but, according to the degree of concentration of the solution of potassium thiocyanate, the shades of colour observed may be blood-red, purple, or brown. Turpentine oil and terpin hydrate also give this reaction. If instead of potassium thiocyanate, a solution of sodium bisulphite is used, but for the rest the reaction is accomplished in the same manner, a beautiful blood-red mixture is obtained.

As other terpene compounds react the same as terpineol, a practical utilisation of this reaction is out of the question.

**Thiosinamine**, the excellent effect of which in cicatrisation after burns, etc., was already mentioned in our last Report<sup>2)</sup>, has lately also been warmly recommended by Mellin<sup>3)</sup>. It is used in

<sup>1)</sup> Pharm. Centralhalle **46** (1905), 971.

<sup>2)</sup> Report October **1905**, 127.

<sup>3)</sup> Accord. to Therap. Monatsh. **12** (1905), 650.

practice in the form of an injection in a 15 to 20 per cent. solution. Injections of 10 per cent. aqueous solution with glycerin are, however, less painful.

**Thymol.** It has no doubt been a surprise to everyone interested in the manufacture of this article, that, according to the new German Customs Tariff, the crude material, i. e. the ajowan-seed which is quite unsuitable for consumption, and which was formerly free of duty, has now been taxed with an import duty of 4 marks per 100 kilos, and has therefore been included among the so-called spice-seeds, such as anise, fennel, caraway, etc. Why this has been done, is inexplicable to the expert, because, as ajowan-seed is exclusively worked up for thymol, and for this purpose is admitted free, and is moreover a tropical product which cannot be grown in Germany, the duty on it will not bring in a single penny, and it would have been better if it had been left duty-free.

The prices of ajowan-seed in India remain firm at about 11/- per cwt.; our heavy old stock was still bought at 8/-, so that we were able to avoid the high quotations of last year.

According to Schill<sup>1)</sup>, thymol is a good remedy against gnats. It is used in the form of a solution of thymol in 50 per cent. alcohol (2:100) which is rubbed on the hands, neck, and face by means of a cotton wool pad or a piece of woollen rag. This keeps the gnats away. Against stings it is recommended to make a paste of bicarbonate of soda and water and apply it to the sting, or to carry it about in a saturated solution and dab it repeatedly on the sting. It is, no doubt, a matter of general knowledge that bicarbonate of soda applied in the same manner, also gives excellent results in slight burns.

**Vanillin.** Jos. Hanuš<sup>2)</sup> reports on the quantitative estimation of vanillin in vanilla extracts. He employs as a suitable reagent for the estimation of vanillin in vanilla, vanilla goods, and vanilla extracts, m-nitrobenzhydrazide, by means of which, in aqueous solution, all the vanillin is precipitated quantitatively. This method is recommended particularly for this reason, that its exactness does not suffer even from the presence of the ordinary adulterants, such as acetanilide, benzoic acid, sugars, or salicylic acid. It is, however, useless if other aldehydes are present, especially piperonal, whose presence in vanillin can be detected by bromine water, with which piperonal rapidly forms needles with a silken lustre.

<sup>1)</sup> Schweiz. Wochenschr. f. Chem. u. Pharm. 1905, No. 24, accord. to Pharm. Centralh. 47 (1906), 157.

<sup>2)</sup> Zeitschr. Untersuch. der Nahrungs- und Genußmittel 10 (1905), 585 to 591. Accord. to Chem. Centralbl. 1906, I. 89.

For the purpose of the determination, liquids are employed which contain 0,05 to 0,15 gm. vanillin. A solution which contains in 10 cc. hot water  $1\frac{1}{2}$  times the theoretically required quantity of m-nitrobenzhydrazide, i. e. 0,1 to 0,25 gm., is added to the vanillin solution; this is left standing in a stoppered vessel with occasional shaking for 24 hours, then filtered through a Gooch's crucible, washed with cold water, dried for 2 hours at 100 to 105°, and then weighed. By multiplying the quantity (in grams) of the weighed condensation-product of the formula



with 0,4829, the quantity of vanillin is obtained. In order to determine the vanillin-content in the vanilla pods, about 3 gm. are extracted for, say, 3 hours with ether (at most 50 cc.), the solvent then evaporated at 60°, next dissolved in 50 cc. water, and, as indicated above, the condensation product of vanillin precipitated with m-nitrobenzhydrazide. As the ethereal extract of vanilla pods contains fat, the reaction mass, in order to remove the fat, is three times extracted with petroleum ether. The petroleum ether solution is passed through the Gooch's crucible, and only then is the vanillin-m-nitrobenzhydrazone placed in the crucible, and washed with petroleum ether previous to drying. In the case of alcoholic vanilla extracts, the alcohol must first be carefully evaporated.

Contrary to Preusse's<sup>1)</sup> observations, Y. Kotake<sup>2)</sup> found in the urine of rabbits to which vanillin had been administered, the presence of a lævorotatory substance. In the animal body vanillin experiences an oxidation into vanillinic acid which is partly separated off in the urine in the form of glycuovanillinic acid. Basic lead acetate precipitates it from its solution. It is lævorotatory, and does not reduce alkaline copper solution. By boiling with dilute sulphuric acid it is split up into vanillinic acid and glycuronic acid.

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**Musk.** A report of Mr. Alexander Hosie<sup>3)</sup>, Consul General at Chengtu, gives some interesting information on the musk-trade. A journey which he undertook in July 1904 on the Eastern borders of Thibet brought him to Tachienlu, the capital of the province Szuchuan, of which one of the most valuable commercial products is musk, which is bartered chiefly for tea, silk, atlas and cloth. At Tachienlu, the

<sup>1)</sup> Zeitschr. f. physiol. Chem. **4** (1877), 213.

<sup>2)</sup> Zeitschr. f. physiol. Chem. **45** (1905), 320. Accord. to Chem. Ztg. Repert. **29** (1905) 328, and Chem. Centralbl. **1905**, II. 690.

<sup>3)</sup> A Journey to Thibet. Chemist and Druggist **67** (1905), 651.

real centre of the trade, the Chinese ounce fetches 10 taels (1 tael = about 2/8). At Chengtu the price is already raised to 18 to 19 taels, but for pure musk as much as 29 to 30 taels are asked. At Szuchuan the musk is already subject to frequent adulterations. In order to detect these, certain definite methods are employed there. If the odour is not satisfactory, or if other doubts exist as to the genuine character, a small incision is made in the musk-bag, a sample taken out, and thrown in water. If the sample remains crumbly, the musk is genuine, but if it dissolves, it is adulterated. Or a sample is placed on a glowing piece of charcoal; if it melts and swells up, the musk is good; if it suddenly becomes hard, it must be regarded as adulterated. The annual sale of musk-bags at Tachienlu for Chinese and foreign markets, is estimated at 1100 to 1200 catties (24533 Chinese ounces, value £ 48750).

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In spite of the great importance of musk in commerce, very little is known of its chemical composition. Total darkness exists especially with regard to the character of the odoriferous substances which alone determine the value of this product. For this reason we considered it opportune to take in hand the solution of this question which is of so much importance both from a scientific and a technical point of view<sup>1)</sup>. In the first place, we determined, by distilling out 500 gm. musk with water-vapour for many days the content of odoriferous substances volatilisable with water-vapour in the natural product. The distillation-water hereby obtained, on which but a small quantity of oil floated, yielded by means of careful extraction with ether a total of 7 gm. of a dark-brown oil with a very unpleasant odour, equal to 1.4% of crude musk oil. The examination of this oil showed that it consists partly of a ketone, which forms a well-crystallizing semicarbazone. From the latter the ketone could again be separated off, by boiling with dilute sulphuric acid, in the form of an oil with a strong musk-like odour. In order to obtain a better knowledge of the properties of the new ketone, large quantities of musk had to be worked up. But it was found convenient to extract the musk first with ether, and then to distil out, with water-vapour, the extract obtained. It was then found that the content of musk oil in various specimens of musk, which to all appearances were of equally good quality, may differ considerably.

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<sup>1)</sup> German Patent application by Schimmel & Co. No. 23255, IV. Cl. 23 a, of 26<sup>th</sup> Jan. 1905. A notice on muskone, abstracted by H. Mann from our circular is published in the *Seifensiederzeitung* **33** (1906), 54; *rep. Chem. Zeitg. Repert.* **30** (1906), 51. Muskone is introduced in commerce as "muskone solution" dissolved in 50 per cent. alcohol, and not (as stated in the report) dissolved in alcohol in the proportion of 50%.

For example from 1 kilo musk, 5 gm. = 0,5% crude musk oil were obtained, and from 3 kilos 21,2 gm. = 0,7%, whilst another consignment yielded 62 gm. = 2,07% oil from 3,051 kilos.

Muskone. The crude musk oil, as obtained by extracting the distillation-water with ether, still contains free fatty acids, and saponifiable constituents (fats). For this reason it was heated, for further purification, for a short time with a small quantity of alcoholic potash, and after separating off and washing with water, fractionated *in vacuo*.

After this treatment 62 gm. crude oil distilled as follows: —

- I. fraction: 65 to 160° at 7 mm. 12,5 gm.
- II. fraction: 160 to 166° at 7 mm. 36,3 gm.

There remained back a fairly considerable, brown residue. After fractionating once more we obtained 37,5 gm. (1,2% of the musk) of a fraction boiling at 145 to 147° at 3 mm pressure, which consisted almost exclusively of the new ketone, for when treated with sodium acetate and semicarbazide hydrochloride, it solidified completely into the solid semicarbazone.

When this principal fraction was once more submitted to distillation, 30 gm. distilled from 142 to 143° at 2 mm. pressure. The remainder passed over up to 145°.

The constants of the ketone were as follows: boiling point 142 to 143° (2 mm. pressure), 327 to 330° (752 mm. pressure),  $d_{15}^{20} 0,9268$ ,  $n_D^{20} 1,47900$ .

This ketone, to which we have given the name "muskone" is the sole bearer of the natural musk-odour. As it has been freed from all disagreeable secondary odours of the musk-secretion, it reproduces the musk-aroma in a hitherto unknown strength and fineness. Muskone is a colourless viscid oil, which is miscible with alcohol in every proportion.

The analysis of muskone gave the following values: —

- I. 0,1202 gm. of the substance: 0,3544 gm CO<sub>2</sub>, 0,1356 gm. H<sub>2</sub>O.
- II. 0,1593 gm. of the substance: 0,4706 gm. CO<sub>2</sub>, 0,1818 gm. H<sub>2</sub>O.

Found:		Calculated for C <sub>16</sub> H <sub>30</sub> O		C <sub>15</sub> H <sub>28</sub> O
I	II			
C 80,41%	80,57%	80,57%		80,25%
H 12,54%	12,68%	12,70%		12,60%

Nitrogen and sulphur could not be detected in the ketone.

With hydroxylamine and semicarbazide, muskone forms crystallising compounds. The semicarbazone is specially characteristic, and suitable for the detection. The latter is obtained by mixing 1 gm. muskone with 1 gm. sodium acetate and 1 gm. semicarbazide hydrochloride with a little alcohol into a paste, and letting it stand for some time. When

water is added, the semicarbazone is precipitated as a white, solid mass, which melts after repeated recrystallisation from alcohol at 133 to 134°. The muskone semicarbazone crystallises in fine, white prisms, which are absolutely odourless. If a trace of it is heated with dilute sulphuric acid, a powerful pure musk-odour soon proclaims that muskone has been split off. The analysis of the semicarbazone gave values on combustion, from which either the formula  $C_{16}H_{31}ON_3$  or  $C_{17}H_{33}ON_3$  can be calculated. Muskone has consequently either the composition  $C_{15}H_{23}O$ , or  $C_{16}H_{30}O$ .

We are at this moment still occupied with the further examination of muskone, and hope to report on this at a later date.

The question whether the natural odoriferous substance of musk is identical with the so-called "artificial musk Baur" (trinitro-isobutyl toluenel and homologues), which is frequently used as a substitute for musk, or with one of its various derivatives, has therefore been brought to a decision by the isolation of muskone. The "artificial musk" has nothing to do with muskone.

With regard to the remaining odoriferous substances of the musk-secretion, they impair by their penetrating, most unpleasant odour the fine muskone-odour to such an extent, that in the musk it cannot be appreciated at its full value. The examination of these compounds, which are partly of a basic character, has not yet been concluded.

**Orris-root, powdered.** Since the prices of Florentine roots have advanced about 12 marks per 100 kilos, and this rise appears to be permanent, we have been compelled to increase our quotations for the well-known fine powder for the present by 10 marks. For the rest we beg to refer to what we have said on this subject under the article "Orris Oil".

**Peru Balsam.** According to Tschirsch<sup>1)</sup> the so-called white Peru balsam of Honduras differs considerably from the genuine white Peru balsam obtained from the fruit of *Myroxylon Pereirae*. It contains, besides free cinnamic acid, a solid resin ester of cinnamic acid, and a mixture of liquid resin ester of cinnamic acid with alcohols, which still require further identification. Tschirsch considers that the white Peru balsam examined by Thoms and Biltz<sup>2)</sup> is not genuine, as it contained free cinnamic acid and cinnamic acid ester of cinnamon alcohol and phenylpropyl alcohol; the genuine balsam does not contain cinnamic acid at all, but on the other hand coumarin.

<sup>1)</sup> Schweiz. Wochenschr. f. Chem. u. Pharm. **43** (1905), 238. According to Pharm. Centralh. **46** (1905), 803.

<sup>2)</sup> Zeitschr. d. allg. Oesterr. Apoth. Ver. **58** (1904), 943. Comp. Report April 1905, 119.

# Notes on recent scientific work concerning terpenes and terpene derivatives.

## General.

In our last October Report (1905, 78) we communicated the results of a study of the laws affecting the composition of a vapour-mixture which is obtained in the distillation of mixtures of liquids. C. v. Rechenberg and W. Weisswange have meanwhile published in the *Journal für praktische Chemie*<sup>1)</sup> the detailed exposition of these researches, under the title of "Distillation of liquids which do not dissolve each other". We would refer to the original work which, in addition to the results already communicated in our Report, contains specially the description of the distillation-experiments with unsaturated oil-vapour in the vapour-mixture.

The influence of odours and perfumes on the health of man is discussed in a report which we abstract from the official organ of the German Union of Samaritans<sup>2)</sup>: —

"It is long since known that certain substances possessing a strong odour are capable of exerting a powerful influence on the human being. The effect differs no doubt considerably in different individuals, but in particularly sensitive persons it may amount to distinct nervous disturbances. It is an indisputable fact, that perfumes or other strong odours affect in a certain manner the nerves and particularly also the mechanism of the respiration, and can thereby cause, for example, nettle-rash and giddiness. Occasionally odours produce a certain impression on the digestive action, and as a consequence cause nausea, vomiting, excessive salivation, and diarrhoea. It cannot be said that odours, whether pleasant or disagreeable, can actually become the cause of a disease in the usual sense, but they can, by influencing the nerves and interfering with their normal action, disturb certain functions which are necessary for the well-being of man, and thereby reduce the body to a condition which is less capable of resisting the attack of a disease. Of course, there are bound to be wide differences between the individual odours and the various human beings. It is a striking fact that people who are occupied in the scavenging of streets, in canalisation work, in slaughter houses, in tanneries, or such places where they are compelled to inhale unlimited quantities of more or less offensive odours, do not find their general condition impaired thereby in any particular way. A contributor to the *Medical Record* calls to mind that the effluvia of manure were for a long time considered an active remedy against rheumatism, and sometimes are so considered even at this day. A proof that pleasant odours also have really an overpowering effect on the human being is found in the well-known example of the tuberose, of which the presence in a room renders many persons positively unconscious. But a whole series of plants could be mentioned whose odours cause headache, such as the honeysuckle, clove, etc. The fragrance of flowering petunias is said to have caused occasionally slight poisoning. The preparation of decoctions of linseed and also

<sup>1)</sup> Journ. f. prakt. Chem. II. 72 (1905), 478.

<sup>2)</sup> Zeitschr. für Samariter- und Rettungswesen 12 (1906), 31.





aqueous mercuric acetate solutions on olefinic compounds, published by him jointly with Paolini, Tonazzi, Cirelli, and others. As we have already reported on the most important parts of the various works<sup>1)</sup>, we content ourselves in this place with a reference to the detailed comprehensive treatment of the "memoria"; we only wish to add, that the glycols  $R \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CH}_3$  formed by the action of mercuric acetate on phenol ethers with propenyl side chain (anethol, isosafrol, methyl isoeugenol), on splitting off water by means of zinc chloride, yield aldehydes. There are not formed (as was at first supposed) the substituted hydratropic aldehydes  $R \cdot \text{CH}(\text{CH}_3) \cdot \text{CHO}$  of Bougault<sup>2)</sup>, as the derivatives (oximes, semicarbazones, acids) show different melting points, but hydrocinnamic aldehydes of the formula  $R \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$ .

### Bibliographical notes.

O. Aschan has published a large work under the title "Chemistry of the alicyclic compounds"<sup>3)</sup>. In this class of bodies, the terpenes and their derivatives, as is well known, occupy the largest space; the book, however, does not confine itself to these, but deals with all hydrated cyclic bodies which have become known up to the present, from trimethylene up to completely hydrated picene. In the general part of this work, the theoretic relations of the alicyclic bodies towards each other have been reproduced in historical order, the fundamental work of v. Baeyer on the hydrobenzene derivatives, his theory of tension, and next in detail the more recent researches on terpenes and camphors commencing with Wallach's work. Separate chapters have been devoted to the influence of the ring-formation on the chemical and physical characteristics of the alicyclic compounds, and also to the stereo-chemistry of these bodies, a field in which not much work has been done up to the present. The special part shows first of all the general manner of formation of the individual hydroaromatic hydrocarbons, alcohols, aldehydes, ketones, acids, and their derivatives, next these bodies themselves, in the order of the number of carbon rings and of the carbon atoms forming them, whereby naturally the terpenes and camphors receive the most detailed treatment.

In this monograph, in which the extremely rich and widely dispersed material is arranged most conveniently and easy of survey, the author has, in his own particular working sphere, created a work which obtains

<sup>1)</sup> Report April 1903, 83; April 1904, 100.

<sup>2)</sup> Thesis, Paris, 1902. Report April 1903, 11. Comp. the present Report page 132.

<sup>3)</sup> Chemie der alicyklischen Verbindungen. Brunswick 1905. Fr. Vieweg & Sohn.

its special value from the criticism interspersed in it, and which will be most welcome particularly to those who wish to make themselves acquainted with the historical development and with the relationship between the individual bodies.

We only wish to refer here to the work published by J. W. Brandel<sup>1)</sup>: "The Volatile Oils 1904", as the interesting parts of the contents have already been communicated in these Reports in the most diverse places.

### Physical notes.

Some time ago Haller<sup>2)</sup> already pointed to the increase in the rotatory power of active bodies, which is caused by attaching a radical such as particular benzylidene, by means of a double-linking. In their last work Haller and March<sup>3)</sup> compare the following partly new bodies and their rotatory powers with each other: benzylidene camphor; hexahydrobenzylidene camphor, colourless crystals of the melting point  $49^{\circ}$  obtained by condensation of hexahydrobenzaldehyde with camphor sodium which had been produced from camphor by means of sodium amide in ethereal solution; benzyl camphor; hexahydrobenzyl camphor obtained by reduction of hexahydrobenzylidene amalgam, boiling point  $192^{\circ}$  at 24 mm. pressure;  $\alpha$ -naphthyl camphor, produced by the action of heptyl iodide on camphor sodium, a colourless oil of the boiling point  $190^{\circ}$  at 25 mm. pressure;  $\alpha$ -naphthylidene camphor by brominating  $\alpha$ -naphthyl camphor and splitting off the hydrobromic acid by means of diethylaniline; boiling point  $180^{\circ}$  to  $182^{\circ}$  at 20 mm. pressure.

Specific rotatory power:

#### a) of the unsaturated bodies

benzylidene camphor	$[\alpha]_D + 425^{\circ} 11'$ ,
hexahydrobenzylidene camphor	„ $+ 131^{\circ} 39'$ ,
$\alpha$ -naphthylidene camphor	„ $+ 136^{\circ} 40'$ ;

#### b) of the saturated bodies

benzyl camphor	$[\alpha]_D + 144^{\circ} 00'$ ,
hexahydrobenzyl camphor	„ $+ 55^{\circ} 07'$ ,
$\alpha$ -naphthyl camphor	„ $+ 51^{\circ} 13'$ .

By this comparison, it is clear that the specific rotatory power of the new hydrated bodies is much lower than that of the corresponding benzene compounds. The rotation of the saturated alkyl derivatives is lower than that of the unsaturated derivatives from which

<sup>1)</sup> Pharm. Review **23** (1905), 321, 339 and 376, **24** (1906), 14 and 39.

<sup>2)</sup> Compt. rend. **140** (1905), 1626.

<sup>3)</sup> Compt. rend. **142** (1906), 316.

they are derived. The nature of the saturated side-chains  $C_6H_{11}$  and  $C_6H_{13}$ , whether they be alicyclic or aliphatic, does not appear to have any appreciable effect on the rotatory power. In benzylidene camphor and its analogues, such as benzyl camphor, it must therefore be the character of the unsaturated benzene nucleus which exerts its influence on the rotatory power of the asymmetric molecule to which it is attached.

### Pharmacologico-physiological notes.

A paper by E. Sack<sup>1)</sup> on odoriferous substances and olfactory sensations, contains interesting information which we can only reproduce here in a few words, as we are only in possession of a short report on the subject. What is usually understood under the expression odoriferous substances, is, chemical individuals which are employed for perfuming objects of use. An exact scientific definition, such as for example that of the idea "dye-stuff", cannot be given of the idea "odoriferous substance". They might possibly be designated as carbon compounds which under certain conditions, whereby a chemical change is excluded, emit a definite characteristic odour. It has often been attempted to group odoriferous substances, like colouring matters, together from certain chemical points of view [Rupe and Majewski<sup>2)</sup>, Klimont<sup>3)</sup>], but when such a group is submitted to a more thorough study, there are found, besides much which is lawful and regular, so many irregularities and exceptions, that it is impossible to carry the principle through. The relationship between the character of the odoriferous substance and the chemical constitution is usually not very easily recognisable, and is frequently of a very complex nature. Above all, one should not be led away too easily by theoretical speculations, as statements in literature on odour-emitting bodies are afterwards very often found to be unreliable. This may possibly in part be explained by the fact that many people are unable to smell correctly, and partly by this, that many bodies which are looked upon as chemically pure, do not possess a pure odour. Occasionally again, odoriferous substances in solid or concentrated form do not possess the characteristic odour which they have when properly diluted. It also happens sometimes that the odour of a body in concentrated form differs entirely from that of the greatly diluted body, so much so, that they might be taken for different bodies. It is well known that the strength of the odour in many substances does not at all stand in simple relation to the degree of concentration or dilution in which the substances occur. Ever

<sup>1)</sup> Chem. Ztg. **29** (1905), 1298.

<sup>2)</sup> Berl. Berichte **33** (1900), 3401.

<sup>3)</sup> Klimont, The synthetic and isolated aromatics, p. 7.

products which are closely allied, in chemical constitution and composition, may differ completely from this point of view. These are all peculiarities which cannot possibly be compared with the conditions prevailing for colouring matters. And for this reason it will hardly ever be possible to speak of a theory of odoriferous substances, in like manner as is now done of a theory of dye-stuffs. The paper concludes with a discussion on the manner in which the sensation of odour is accomplished, and on the methods by which odours are tested and compared with each other. In the last-named work a good memory for the individual odours is very useful, and this can be very much perfected by constant practice.

From Vandeveld<sup>1)</sup> originates a biological method for the determination of the toxic action of chemical compounds, which has assisted in the examination of alcohols and of essential oils and some of their constituents<sup>2)</sup>. The principle of his method is based on this, that essential oils in definite quantities bring about hæmatolysis in defibrinated bullock's blood floating in the proportion of 5 per cent. on normal solution of common salt. The test is made in this manner, that to 2,5 cc. of a 5% suspension of defibrinated bullock's blood in normal solution of common salt (0,9% NaCl), are added together 2,5 cc. of a mixture of normal solution of common salt and of a solution of 0,05 gm. of the oil to be examined, in 100 cc. of 50 per cent. alcohol (with 0,9% NaCl). According to the content of essential oil or of the 50% aqueous-alcoholic solution, in the last-named 2,5 cc. mixture, hæmatolysis occurs sooner or later in the total mixture (5 cc.), and by eliminating the known hæmatolytic action of the alcohol, the share of the essential oil in the hæmatolysis can be determined numerically, and its relation as isotoxic value to the unit of weight of alcohol fixed. According to this, the so-called "fruit oils", strawberry, raspberry, apple and other oils, possess the most feeble hæmatolytic action, 4,78 gm. as compared with 100 gm. absolute alcohol; the next in the series are peach and bitter almond oils, and benzaldehyde, with 2,33 gm., nitrobenzene and carvone with 1,10 gm., whilst finally anethol, anise oil, and star-anise oil reach the highest isotoxic value with 0,20 gm. Vandeveld hopes to be able to base a new bio-chemical method for the determination of essential oils in alcoholic beverages on his process.

We feel bound to qualify the name "fruit oils" as indistinct, inasmuch as it is not clear whether it applies to the natural oils, or

<sup>1)</sup> Chem. Ztg. **29** (1905), 975.

<sup>2)</sup> Bull. de l'Assoc. Belge des chimistes **17** (1903), 269; 208. Report October 1904, 102.

to the artificial fruit essences (esters of certain fatty acids). In this connection it is curious that peach "oil" does not take its place among the "fruit oils", but on the contrary shows the isotoxic value of benzaldehyde, whilst on the other hand cognac oil, natural and artificial, figure at the other end of the series with 0,28 and 0,22 respectively. In the case of bitter almond oil, it might not be altogether unimportant, whether it is used free or not from hydrocyanic acid. It appears questionable whether this method is suitable as a method of determination, in view of the frequently extremely minute quantities of essential oils in liqueurs, especially when it is taken into consideration that in the majority of liqueurs it is a question of mixtures of essential oils.

Galewsky<sup>1)</sup> recently observed a case, in which a lady suffered from inflammation with red spots like nettle-rash, accompanied by severe itching, on the parts of the neck which were not covered by the dress, and which was clearly due to the fact that she had been staying in a room which was decorated with eucalyptus shrubs. The same eruption appeared already after half an hour in a girl who had rubbed the shrubs on the skin.

### Phyto-physiological notes.

In a previous work Charabot and Hébert<sup>2)</sup> have studied the influence exerted by the development of the inflorescences on the essential oil of the green organs of sweet basil (*Ocimum basilicum*), and a recent communication of the same authors<sup>3)</sup> deals with the effect of the blossoms which perform their function, on the odoriferous substances.

A bed of sweet basils was divided in two parts, of which one contained the experimental plants, and the other the control plants. From the former, the newly formed inflorescences were from the commencement of the flowering season removed every day and weighed, and extracted with petroleum ether, in order to determine the total quantity of essential oil produced. At the commencement of the experiments, a trial cut was made, and the state of development of the plants, their oil-content, and the composition of the oil determined. When the fructification was completed, the control plants were cut, and the green parts distilled and the inflorescences extracted with petroleum ether. The extract was then submitted to distillation with water vapour. On the same day the experimental plants were also distilled, and the same took place with the extract obtained during

<sup>1)</sup> Dermatol. Zeitschr. **1905** No. 1; According to Pharm, Centralh. **46** (1905), 968.

<sup>2)</sup> Compt. rend. **138** (1904), 380; Bull. Soc. Chim. III. **31** (1904), 402.

<sup>3)</sup> Compt. rend. **141** (1905), 772; Bull. Soc. Chim. III. **33** (1905), 1121.

the experimental period by means of petroleum ether from the blossoms cut off. A comparison of the results obtained showed the following: The removal of the inflorescences causes a considerable increase in the weight of the plant, up to 39% of the normal weight. The quantity of oil of any individual plant has almost doubled, the increase amounting to up to 82% of the normal production. The older inflorescences which have accomplished their function have retained less odoriferous matter than the inflorescences cut off had taken away. The absolute weight of the oil remaining behind in the green parts of each plant has increased, but this increase is not proportionate to their development. This is due to the fact that, whilst in the control plants after completed fructification a certain quantity of oil returns<sup>1)</sup> to the parts containing chlorophyl, this return cannot take place in the experimental plants, as they have been systematically deprived of their inflorescences. On the other hand, the authors found that the comparative quantity of oil is also larger in the experimental plants, which may be explained thus, that in the inflorescences which have remained on the plants, essential oil has been consumed in the fructification process<sup>2)</sup>.

The observations made also explain why the peppermint<sup>3)</sup> which has been changed by the stings of insects and which has lost the capacity of developing blossoms, shows a considerable increase in the development of the green organs and an important augmentation in the oil production.

On the formation and distribution of essential oil in the sweet orange during its development, Roure-Bertrand Fils<sup>4)</sup> have made researches of which the result may be summed up in the following: The formation of essential oils is brisker in the young organs of the plant than in those which are already fully developed. The stalk is noticeably poorer in odoriferous substances than the leaf, and it especially contains considerably less citral. The quantity of essential oil remaining behind in the stalk diminishes constantly.

Bourquelot and Danjou<sup>5)</sup> have continued their examinations of the glucoside contained in the common elder (*Sambucus nigra* L.), to which we referred in our last Report<sup>6)</sup>. 1 Kilo fresh leaves, macerated

<sup>1)</sup> Charabot and Laloue, Compt. rend. **139** (1904), 928 and **140** (1905), 667. Comp. Report October **1905**, 90.

<sup>2)</sup> Compt. rend. **140** (1905), 667. Comp. Report October **1905**, 90.

<sup>3)</sup> Comp. the report under Peppermint oil, p. 54.

<sup>4)</sup> Reports of Roure-Bertrand fils, Grasse, October **1905**, 21.

<sup>5)</sup> Journ. de Pharm. et Chim. VI. **22** (1905), 210.

<sup>6)</sup> Journ. de Pharm. et Chim. VI. **22** (1905), 154. Report October **1905**, 110.

with water with emulsin added, yielded 0,142 gm. hydrocyanic acid. The alcoholic extract from 1 kilo leaves, after removal of the alcohol and substitution of the latter by water after invertin and emulsin had been added, yielded 0,156 gm. hydrocyanic acid. In the fresh leaves and also in the other organs of common elder, the authors detected invertin; the blossoms contain most of it, whilst the young fruit appears to have the smallest content. Small quantities of emulsin are also present in the leaves, blossoms, and fruit. In addition to two varieties of *Sambucus nigra*, which also contained the glucoside, the authors examined *Sambucus racemosa* L. and *Sambucus Ebulus* L., but in neither of these could a glucoside be detected. But possibly the latter may contain another body which can be split up by emulsin. In the further course of the examination, Bourquelot and Danjou<sup>1)</sup> succeeded in obtaining in crystalline form the glucoside which they had hitherto not been able to produce in the pure state. It crystallises in long colourless needles, is odourless and has a slightly bitter taste. It is readily soluble in water, cold alcohol, and acetic ether, almost insoluble in ether; it softens at 149° and melts at 151 to 152°. It is optically active ( $[\alpha]_D - 76,3^\circ$ ), does not lose weight when heated to 100°, and does not reduce Fehling's solution. The hitherto unknown glucoside which resembles amygdalin, and which the authors have named sambunigrin, is split up by emulsin into glucose (61,28%), hydrocyanic acid (8,61%), and benzaldehyde; it appears to be isomeric with the amygdonitril glucoside  $C_{14}H_{17}NO_6$  of E. Fischer. In a further work Bourquelot and Danjou<sup>2)</sup> describe in detail the production, purification and properties of sambunigrin. It should still be mentioned\* that the glucoside can also be split up by the ferment of *Aspergillus niger*, and that, as a matter of fact, the above-mentioned formula  $C_{14}H_{17}NO_6$  belongs to it.

Stimulated by this work, L. van Itallie<sup>3)</sup> has again taken up his earlier investigations on the presence of hydrocyanic acid in plants and he was not only able to confirm the results of Bourquelot and Danjou, but also became acquainted with a new occurrence of hydrocyanic acid. In the leaves of *Thalictrum aquilegifolium* L. he detected in 100 gm., 0,05 to 0,06 gm. hydrocyanic acid, in 142 gm. twigs he found 0,0044 gm., but in 200 gm. roots no trace of hydrocyanic acid at all. The leaves of *Thalictrum flavum* L., *Thalictrum minus* L. and *Thalictrum glaucum* did not contain hydrocyanic acid. The acid originates from a glucoside which, like the phaseolunatin discovered by Dunstan and Henry in *Phaseolus lunatus* L., can be split up

<sup>1)</sup> Ibidem p. 219. Compt. rend. **141** (1905), 598.

<sup>2)</sup> Journ. de Pharm. et Chim. VI. **22** (1905), 385.

<sup>3)</sup> Ibidem p. 337.

into acetone and hydrocyanic acid. Apart from the glucoside, the author detected in *Thalictrum aquilegifolium* an enzyme, which is capable of decomposing both the glucoside found and amygdalin.

Another new glucoside, prulaurasin, has been isolated by H. Hérissé<sup>1)</sup> from the leaves of the cherry laurel (*Prunus lauro-cerasus* L.). By extracting the leaves with boiling water, evaporating the bulk of this *in vacuo*, diluting the residue with alcohol, filtering, driving off the alcohol *in vacuo*, and purifying the residue, he obtained the body in a crystalline state. It crystallises in thin colourless needles, has a slightly bitter taste, melts at 120 to 122°, is readily soluble in water, alcohol, acetic ether, almost insoluble in ether, and turns the plane of polarised light to the left ( $[\alpha]_D - 62,69^\circ$ ). Emulsin splits up prulaurasin into hydrocyanic acid (8,59%), glucose (61,24%), and benzaldehyde. It has the formula  $C_{14}H_{17}NO_6$ , and is isomeric with the amygdonitril glucoside of E. Fischer<sup>2)</sup> and the above-mentioned sambunigrin of Bourquelot and Danjou. It differs from these two by its solubility, its melting point, and its optical rotatory power.

According to L. Guignard's<sup>3)</sup> examinations, the red currant bush (*Ribes rubrum* L.) also contains small quantities of a glucoside splitting off hydrocyanic acid. From 100 gm. leaves were obtained: in June when the currants were still green, 0,0035 gm. hydrocyanic acid; a few weeks later, when they were ripe, 0,0026 gm., and in the beginning of August only 0,0015 gm. In 100 gm. of the young branches which only contained little chlorophyl, only small quantities could be detected, and in an equal weight of roots and the ripe fruit no trace of hydrocyanic acid could be found. Of other species of *Ribes*, *Ribes aureum* Pursh., behaved the same as *Ribes rubrum*; the quantity of glucoside was only smaller. The leaves of *Ribes nigrum* L., *Ribes uvacrispa* D. C., *Ribes sanguineum* Pursh., *Ribes multiflorum* Kit., *Ribes subvestivum* Hook. et Arn., *Ribes prostratum* L'Hér., and *Ribes Gordonianum* Lem., yielded no hydrocyanic acid. In the leaves and twigs containing glucoside, and in the roots and fruit free from glucoside of *Ribes rubrum* and *Ribes aureum*, the author detected emulsin, and the like in the species *Ribes nigrum* and *Ribes uvacrispa* which contain no glucoside at all. Of seeds, only those of *Ribes rubrum* and *Ribes nigrum* were examined, and in them the presence of emulsin was proved.

The examination of prulaurasin compelled Hérissé<sup>4)</sup> to determine small quantities of benzaldehyde. For the separation of the

<sup>1)</sup> Compt. rend. **141** (1905), 959, and Journ. de Pharm. et Chim. VI **23** 906), 5.

<sup>2)</sup> Berl. Berichte **28** (1895), 1508.

<sup>3)</sup> Compt. rend. **141** (1905) 448.

<sup>4)</sup> Journ. de Pharm. et Chim. VI. **23** (1906), 60.

aldehyde he employed phenylhydrazin, filtered off the phenylhydrazon formed, and after drying weighed it. He made use of pure crystallised amygdalin for controlling the process. A weighed quantity of the last named substance was mixed with 60 cc. water and with sufficient emulsin to complete the decomposition of the glucoside in 2 to 3 days at 15 to 20°. He then distilled 50 cc. off from the mixture, and mixed the distillate with 50 cc. of a solution which contained in 100 cc., 1 cc. freshly distilled phenylhydrazin and 0,5 cc. glacial acetic acid, so that a large excess of phenylhydrazin was present. He then heated for 20 to 30 minutes in a boiling water bath, and after 12 hours filtered the phenylhydrazon formed in a Gooch's crucible, washed with 20 cc. cold water and dried in a vacuum exsiccator. In five estimations with constantly diminishing quantities of amygdalin, he thus found in amygdalin an increasing content of 21,09 to 22,5 % benzaldehyde, whilst theoretically 23,19 % are required. Hérissé recommends that in carrying out the determination only such quantities of benzaldehyde should be used, as yield 0,1 to 0,25 gm. phenylhydrazone, and for the rest to follow the course indicated for amygdalin.

A contribution to the knowledge of the essential oils of the Hepaticæ by Karl Müller<sup>1)</sup> is intended to supply a further proof that the view of Pfeffer<sup>2)</sup> which at present is still generally accepted, that the oil bodies of the Hepaticæ consist chiefly of fatty oil with small admixtures of protein substances and water, is erroneous. The author examined only *Jungermanniaceæ*, viz., —

1. *Mastigobryum trilobatum* L. This hepatica when dried in the air loses 90 % of its weight, and yields on rational steam-distillation 0,93 % of the dry substance of an orange-yellow essential oil, which resembles in the odour sandal and cedarwood, but at the same time reminds of the odour of pine-needles  $d_{15}^0$  0,945 to 0,947 (a sample distilled with a bad yield had  $d_{15}^0$  0,975);  $[\alpha]_D + 12,88$  (determined with undiluted oil); saponification number 5,4. On saponification, an acid mass, semi-solid at 16°, was obtained, which yielded a white lead salt, soluble in ether. The bulk of the oil boiled at 260 to 270°. The distillate had a blue-green colour,  $d_{20}^0$  0,946  $[\alpha]_D + 25,59$ °; it contained 87,06 % C and 12,65 % H. When this principal fraction was oxidised with chromic acid and glacial acetic acid, a body  $C_{10}H_{16}O$  was obtained (boiling point 260°), and for this reason the author attributes to the crude material the terpene formula  $C_{10}H_{16}$ . The last runnings of the oil (boiling point 27

<sup>1)</sup> Zeitschr. f. physiol. Chem. 45 (1905) 299 Accord. to Chem. Centralbl. 1905, II, 768. Comp. also Report April 1904, 106.

<sup>2)</sup> The oil bodies of the hepaticæ, "Flora" 1874, No. 1 to 3.

to  $285^{\circ}$ ) contained 5.4% oxygen, and had the specific rotation  $[\alpha]_D +42,21^{\circ}$  (determined in 3,9 per cent. alcoholic solution).

2. *Leioscyphus Taylori* Hook. This moss dried at  $100^{\circ}$  and pulverised, yielded 1,6% viscid, blue-green, essential oil with a very intense, persistent, peculiar odour, and a very unpleasant taste;  $d_{20} 0,978$  and  $0,986$ ;  $[\alpha]_D -3,44^{\circ}$  (determined in 9,03 per cent. alcoholic solution); saponification number 11,4. The analyses of the fraction of the boiling point  $260$  to  $265^{\circ}$ ,  $d 0,937$ ,  $[\alpha]_D -22^{\circ}$  (?) agreed with a sesquiterpene alcohol  $C_{15}H_{26}O$ . The fraction of the boiling point  $265$  to  $278^{\circ}$  appears to contain a terpene  $C_{15}H_{24}$ . The fraction of the boiling point  $280^{\circ}$  to  $290^{\circ}$  ( $[\alpha]_{\text{white}} +26,88^{\circ}$ ) contains a sesquiterpene alcohol  $C_{15}H_{26}O$ . Solid benzoyl compounds could not be obtained from either alcohol.

3. *Madotheca levigota* Schrad. The moss dried in the air yielded 0,9% of a comparatively mobile, orange-yellow oil with a pleasant odour;  $d_{16} 0,856$ ;  $[\alpha]_D +72,74^{\circ}$ ; saponification number 5,56. The peppermint-like taste of the moss does not originate from the essential oil. The fraction of the boiling point  $150$  to  $160^{\circ}$  (17 mm. pressure)  $d_{15} 0,968$ ,  $[\alpha]_D +132,23^{\circ}$ , boils at atmospheric pressure with decomposition at  $280^{\circ}$ , and contains an alcohol  $C_{10}H_{18}O$ .

4. *Alicularia scalaris* Corda. The oil of this hepatica is lemon-yellow, and reminds in the odour of the fragrance of the forest;  $d_{15} 0,965$ ;  $[\alpha]_D -33,49^{\circ}$ .

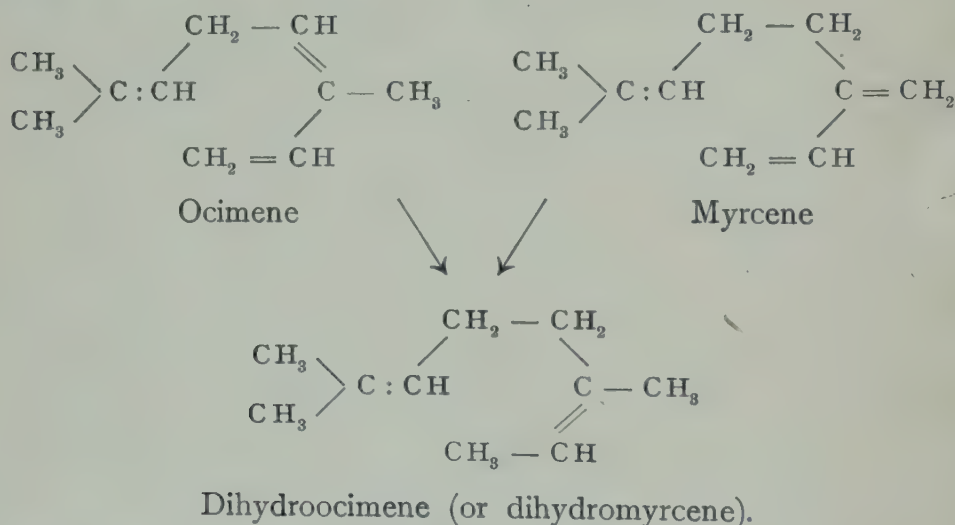
## Hydrocarbons.

Myrcene, Ocimene. The number of the olefinic terpenes which have become known up to the present is but small. The member of this class first described in the year 1891, the artificially produced anhydrogeraniol of Semmler, has not been examined further; but there are numerous communications in existence dealing with the two olefinic terpenes myrcene and ocimene which occur naturally.

Enklaar<sup>1)</sup> has set himself the task of clearing up the relationship between these two bodies. The ocimene was produced from the leaves of *Ocimum basilicum* L., in a yield of 0,37%, and obtained by suitable treatment as an oil of the specific gravity 0,8031,  $n_{D18} 1,4857$ . The myrcene, which we had placed at the author's disposal for the purpose of this examination, had after purification  $d_{15} 0,8013$ ,  $n_{D19} 1,4700$ . Whilst ocimene, under unfavourable conditions, hardly changed after 4 years, myrcene had almost entirely become resinified after 2 years, in spite of the fact that light and air had been excluded. The two terpenes, which were beyond doubt identified as different substances,

<sup>1)</sup> Over Ocimen en Myrceen, eene bijdrage tot de kennis van de aliphatische terpenen. Thesis, Utrecht, 1905.

yielded on reduction with sodium and alcohol the same product of hydration, i. e., a hydrocarbon  $C_{10}H_{18}$  with two double linkings, and had the following constants: boiling point  $166^{\circ}$  to  $168^{\circ}$  (at 761 mm. pressure),  $n_{D17^{\circ}} 1.451$ , molecular refraction found 47.62, calculated 47.34. The specific gravity of the dihydro-terpene from ocimene was 0.779; the one obtained from myrcene was higher, namely 0.785, probably owing to the presence of some unchanged myrcene. The identity of the two products of reduction was further shown by the identity of the tetrabromides of the melting point  $88^{\circ}$  produced from them. It is therefore accepted as an established fact, that both ocimene and myrcene are olefinic terpenes with three double linkings, of which one can be saturated off by hydration, and the two others by the addition of bromine. Different oxidation experiments with ocimene yielded as characteristic compound malonic acid, and from this, as also from the results of the reduction on the strength of Thiele's views concerning the so-called conjugated double-linkings Enklaar deduces for the two terpenes the following formulæ: —



By hydration according to Bertram-Walbaum's method, there was formed from myrcene the optically inactive alcohol  $C_{10}H_{18}O$ , myrcenol, which Power and Kleber consider identical with linalool, but which is thought to be different from the latter by Barbier, Semmler and others. By comparison with the phenyl urethane of linalool which was first produced in our laboratory<sup>1)</sup>, and which he examined particularly for its optical activity, Enklaar demonstrated that the two alcohols are different, although the melting points of their phenyl urethanes lie only 2 to  $4^{\circ}$  apart. Myrcenol phenyl urethane melted at  $68^{\circ}$ , the urethane of the optically active linalool

<sup>1)</sup> Report October 1902, 70.

at  $64^{\circ}$ , and of the racemic linalool at  $66^{\circ}$ . For linalool, Tiemann-Semmler's formula could be confirmed. The corresponding ocimene yielded a phenyl urethane of the melting point  $72^{\circ}$ .

When heated in a reflux-condenser, ocimene is converted (according to van Romburgh) into an isomeric "alloocimene"; Enklaar considers the latter a geometric-isomeride, as it yields on reduction the same dihydro product as ocimene. Attempts made to arrive at the corresponding alcohol by hydration with glacial acetic acid and sulphuric acid failed and led back again to ocimene.

Pinene. Concerning this terpene, Kondakow<sup>1)</sup> gives a historical retrospect of the development of the formulæ drawn up for pinene by Kannonikow, Wallach, Bredt, v. Baeyer and Wagner. But while the structure of pinene itself has now become clear, this is not yet the case with regard to the reaction-mechanism of the principal conversions. A distinction must be made whether the reaction occurs with the double-linking, or with the diagonal linking of pinene. Thus, in the oxidation into pinene glycol and into pinol, the latter appears to be split asunder and the double linking to remain intact. In view of the spatial arrangement of the pinene molecule, a direct conversion from the glycol to pinol with loss of water might be accepted. On the other hand, in the treatment with acids, in attaching HCl, etc., the bridge linking remains intact, and the reactions takes place with the double linking. Kondakow includes in this the formation of pinene hydrochloride and its isomerides, of pinene dibromide, and also of terpeneol, whereby  $\text{SO}_4\text{H}_2$  is said to attach itself to the double linking, with erection (Kondakow says not quite correctly "splitting-off") of the isopropyl-group, and in which subsequently the ester and finally the alcohol itself is formed<sup>2)</sup>. According to Kondakow, the formation of the terpeneol derivatives occurring naturally results in a similar manner. The occurrence of isomeric additional compounds is explained partly by re-grouping of the additive atom-arrangements in the finished product, and partly by their entrance at various places in the picean ring. This appears to be proved by the behaviour of the as yet little examined alcohol pinanol [pino camphol]<sup>3)</sup>.

With regard to the behaviour of pinene while being brominated, and the occurrence of cyclene, the opinions have not yet become

<sup>1)</sup> Chem. Ztg. **29** (1905), 1225.

<sup>2)</sup> Kondakow's ideas about the reaction-process are, in our opinion, not very clearly expressed.

<sup>3)</sup> Whether, as Kondakow supposes, a migration of the carbon linkings in the HCl addition product of this alcohol, with formation of bornyl chloride and Fenchyl chloride, actually takes place, will have to be proved by the further experiments which are announced.

settled, as the views of Wagner, Semmler and Kondakow on the course of the reaction have not been strictly proved, and contradict each other.

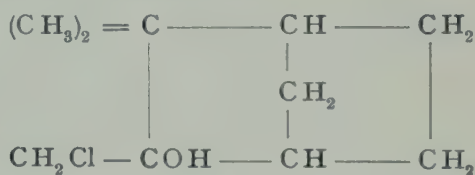
In distilling the xanthogenic acid ester of Wallach's pino-campheol<sup>1)</sup> according to the usual method, A. Tschugaeff and A. Esche<sup>2)</sup> observed between 180° and 190° a very energetic decomposition. The reaction took place according to the following equation:



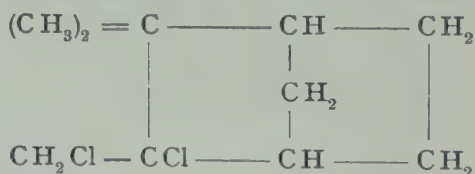
The hydrocarbon formed, after distillation in a current of vapour, shaking with potash liquor, and purification over sodium, was found to be pure pinene of the boiling point 155° to 156°. The melting point of its nitrosochloride was found at 103°.

Camphene. According to K. Slawinski's<sup>3)</sup> examinations camphene combines with hypochlorous acid, with formation of the following products:

1. Camphene glycol chlorhydrin



2. The chloride  $C_{10}H_{16}Cl_2$  of the melting point 139° to 140°,



3. A mixture of three isomeric monochlorides  $C_{10}H_{15}Cl$ , which consists of camphene monochloride, cyclene monochloride, and an unknown chloride.

From his examination the author draws the conclusion that the structure of isoborneol and camphene is the same.

Phellandrene. J. Kondakow and J. Schindelmeiser<sup>4)</sup> have attempted to produce phellandrene synthetically from carvomenthene.

<sup>1)</sup> Liebig's Annalen **300** (1898), 288. Report October **1898**, 54.

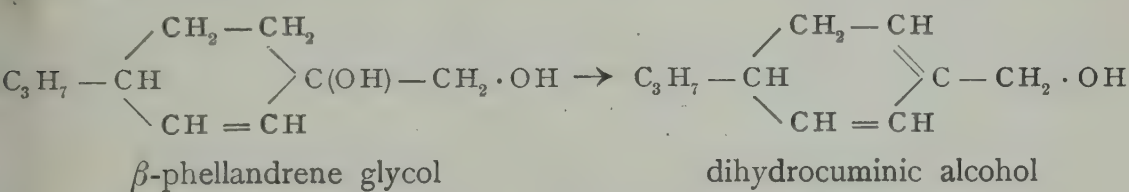
<sup>2)</sup> Accord. to Chem. Ztg. **29** (1905), 1189.

<sup>3)</sup> Bull. Intern. Acad. Cracovie **7** (1905), 491. Acc. to Chem. Ztg. Repert. **29** (1905), 378.

<sup>4)</sup> Journ. f. prakt. Chemie II. **72** (1905), 193.

They converted carvomenthene, according to Reychler's method, into tertiary carvomenthol, and the latter, through the chloride (boiling point 83,5 to 84,5° at 12 mm. pressure,  $d_{40}^{20} 0,932$ ) into tertiary carvomenthene (boiling point 174 to 176°;  $d_{40}^{20} 0,811$ ;  $n_D 1,45709$ ). From this the dibromide was produced, and from the last-named body was obtained, by the action of alcoholic potash, a hydrocarbon of which the bulk boiled at 175° to 180° ( $d_{40}^{20} 0,825$ ;  $n_D 1,46693$ ), whilst the smaller portion ( $d_{40}^{20} 0,828$ ;  $n_D 1,4673$ ) passed over at 180° to 185°. Both fractions are inactive. The authors believe that their hydrocarbon (which is not uniform) either has the constitution of Semmler's<sup>1)</sup> phellandrene, or is isomeric with it. In order to compare it with natural phellandrene, the authors produced the as yet little known halogen addition products of d-phellandrene from oil of water fennel. By the action of hydrochloric acid in a solution of glacial acetic acid, they obtained a product which could by fractionating be split up into a solid monochloride  $C_{10}H_{17}Cl$  (boiling point 86° at 11 mm. pressure, melting point about 110°; dextrorotatory) and a liquid dichloride  $C_{10}H_{18}Cl_2$  (boiling point 122,5 to 125° at 16 mm. pressure;  $d_{40}^{20} 1,006$ ;  $n_D 20^\circ 1,48516$ ).

According to Wallach's<sup>2)</sup> examinations,  $\beta$ -phellandrene of water-fennel oil is converted by oxidation with potassium permanganate into a glycol which, by loss of water, yields tetrahydrocuminic aldehyde. Wallach<sup>3)</sup> has now, in addition to this body, also observed the presence of dihydrocuminic alcohol, which can also be formed when water is split off:



As, besides  $\beta$ -phellandrene, tetrahydrocuminic aldehyde is present in water-fennel oil itself, Wallach<sup>4)</sup> endeavoured to determine whether the readily oxidisable hydrocarbon could be converted by oxidation with free oxygen in the presence of water, into the aldehyde mentioned above.  $\beta$ -Phellandrene was shaken in sunlight with an equal quantity of water, in a flask filled with oxygen. There was then obtained, besides 35 to 36% of unconverted phellandrene, not the expected

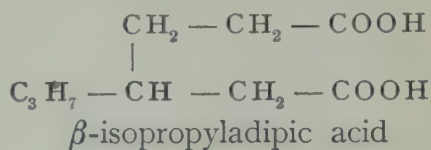
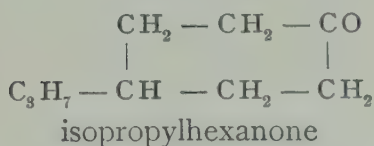
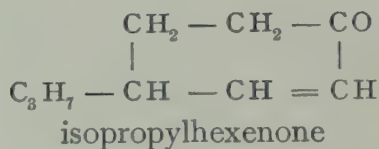
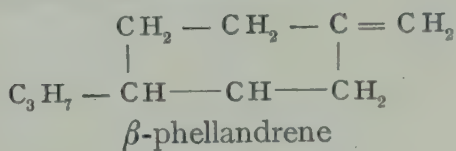
<sup>1)</sup> Berl. Berichte **36** (1903), 1749.

<sup>2)</sup> Liebig's Annalen **340** (1905), 1. Report October 1905, 97.

<sup>3)</sup> Liebigs Annalen **343** (1905), 37.

<sup>4)</sup> Ibidem p. 29.

tetrahydrocuminic aldehyde, but 5 to 10% (calculated as semicarbazone) of a ketone  $C_9H_{14}O$  (boiling point  $103$  to  $106^\circ$  at 15 mm. pressure,  $220$  to  $224^\circ$  at atmospheric pressure;  $d_{0.9387}$ ;  $n_{D26} 1.4788$ ), which possessed an odour greatly resembling that of the aldehyde and whose semicarbazone melts at  $183$  to  $184^\circ$ . The unsaturated ketone combines with sodium bisulphite, and in alcoholic-ammoniacal solution with sulphuretted hydrogen into a sulphur compound which melts at  $121$  to  $122^\circ$ . It can be reduced with sodium and alcohol or moist ether to a saturated alcohol, which can be oxidised to a saturated ketone  $C_9H_{16}O$ , which again is split up by chromic acid into  $\beta$ -isopropyl adipic acid. It follows from this that the ketone  $C_9H_{14}O$  formed from  $\beta$ -phellandrene by oxidation with free oxygen, is  $\Delta_2$ -isopropyl-(1)-hexenone-(4):



The progress of the oxidation shows that the oxidation of unsaturated compounds by means of free oxygen proceeds in a totally different manner from that with potassium permanganate. Whereas, if the last-named agent is employed, it commences with the addition of hydroxyls, in the "autoxidation" superoxides are first of all formed, with absorption of oxygen. Of both oxidising agents the semicyclic linking is more readily attacked than the purely cyclic one.

Isopropyl-(1)-hexenone-(4) could (as Wallach surmised) also be obtained from the above-named glycol by oxidation with chromic acid.

The odour of the ketones produced by Wallach induces him to believe that the position of the oxygen towards the isopropyl-group influences the odour of cyclic ketones in such manner, that the ortho-position brings about the odour of menthone, the meta-position that of carvone, and the para-position a cuminal-like odour.

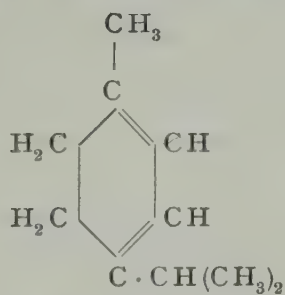
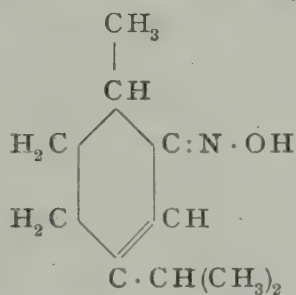
The base<sup>1)</sup> previously obtained by reduction of nitro- $\beta$ -phellandrene of which it was still doubtful whether it was a di- or a tetrahydrocuminylamine, was now recognised as identical with the tetrahydro base which can be produced from tetrahydrocuminaldoxime.

Semmler's proposal, to designate the terpenes which, like- $\beta$ -phellandrene, contain a semi-cyclic  $:CH_2$ -group, as *pseudo* terpenes, is

<sup>1)</sup> Liebigs Annalen **340** (1905), 8; Report October 1905, 97.

not accepted by Wallach<sup>1)</sup>, as just these terpenes are not "false", but are specially characteristic. But as the need is felt to give a name to this :C H<sub>2</sub>-group, which for example is present in limonene, carvone, citronellal, isopulegone, and the phenols examined by Auwers and Zincke, he calls it "methene".

Terpinene. T. Amenomiya<sup>2)</sup> supplies a contribution to the constitution of terpinene with the continuation of his studies<sup>3)</sup> of the nitro-nitrosite of this terpene. If 5 gm. of this compound with 50 cc. 75 per cent. alcohol and 15 gm. zinc dust are heated to boiling, a brisk reaction takes place, with development of nitrous acid. When water is added, a syrup is precipitated, which finally becomes solid. When distilled in a current of steam, a colourless oil passes over which soon becomes crystalline. The product purified with methyl alcohol melts at 91 to 92°, and proved to be carvenone oxime. The melting point of the semicarbazone of the carvenone obtained from it lies at 204°. In the same manner terpinene nitrosite can be reduced. According to this result one feels inclined to believe that terpinene must be the carvenene which is derived from carvenone:



Although the above result renders it probable that terpinene nitronitrosite has the same carbon arrangement in respect of the position of the double linkings, as terpinene, and that therefore during the treatment with nitric acid a migration of the double linking from  $\Delta^4$  to  $\Delta^3$  has not taken place, this does not settle the question whether the very small quantity of carvenone oxime from the nitrosite must not be considered as a product of conversion during the reduction. But it may now be concluded from the formation of carvenone oxime, that in the terpinene molecule a double linking is in the  $\Delta^1$  position. It would be a matter of interest to try whether a hydrocarbon can be produced from carvenone which is identic with terpinene.

<sup>1)</sup> Liebig's Annalen **343** (1905), 28.

<sup>2)</sup> Berl. Berichte **38** (1905), 2730.

<sup>3)</sup> Berl. Berichte **38** (1905), 2022; Report October 1905, 100.

J. Houben<sup>1)</sup> reports on syntheses of aromatic carboxylic acids by means of Grignard's reaction. It is a well known fact that, according to V. Grignard, carboxylic acids can readily be obtained by allowing carbon dioxide to act on the organomagnesium salts, and decomposing the intermediate products formed with dilute sulphuric acid:  $R \cdot MgX + CO_2 = R \cdot CO \cdot OMgX$ ;  $R \cdot COOMgX + H_2O = R \cdot COOH + HO \cdot MgX$ .

Already in 1902, J. Houben and L. Kesselkaul<sup>2)</sup> have employed this method for the production of aromatic and hydroaromatic carboxylic acids. The work under review gives the composition of a few syntheses in the series of aromatic and hydroaromatic carboxylic acids. First of all Houben describes the action of magnesium and p-dibromobenzene in ethereal solution in the presence of a small quantity of methyl iodide. By allowing carbon dioxide to act on the reaction mass, he obtained terephthalic acid in addition to p-bromobenzoic acid and p-dibrom-acetophenone.

Hydropinene carboxylic acid  $C_{10}H_{17} \cdot COOH$ , he obtained in a yield of about 40%, by pouring on 14 gm. magnesium in about 100 cc. absolute ether, a concentrated ethereal solution of 100 gm. solid pinene hydrochloride  $C_{10}H_{17}Cl$ , to which a small quantity methyl iodide has been added. After several days, dry carbon dioxide is introduced into the reaction mass. Next, the mass is decomposed with ice and dilute mineral acid, and from the ethereal layer the acid is isolated with soda solution. Hydropinene carboxylic acid boils at atmospheric pressure at  $268^\circ$ , at 13 mm. pressure at  $153^\circ$ ; melting point  $72$  to  $74^\circ$ . It is a monobasic acid of the formula  $C_{11}H_{18}O_2$ .

The corresponding anhydride (hydropinene carboxylic acid anhydride  $C_{22}H_{34}O_3$ ) is formed fairly quantitatively when the acid is boiled for half an hour with ten times the weight of acetyl chloride. It crystallises from alcohol in silky brilliant feathers of the melting point  $211$  to  $212^\circ$ .

Hydrodicamphene.  $C_{10}H_{17} \cdot C_{10}H_{17}$ , is formed by the action of magnesium on pinene hydrochloride in ethereal solution, according to Wurtz's synthesis, in a yield of 19 to 22%, when 2 molecules pinene hydrochloride act on 1 molecule magnesium with formation of magnesium chloride and hydrodicamphene. It crystallises from alcohol in feathery crystals of the melting point  $74$  to  $75^\circ$  and boiling point  $322$  to  $323^\circ$ . It is scarcely attacked by concentrated sulphuric acid and by chromic acid. At 12 mm. pressure it distils at  $180^\circ$  to  $190^\circ$  as a water-white liquid, and appears to be identical with the hydrocarbon  $C_{20}H_{34}$ , produced by A. Etard and G. Meker<sup>3)</sup>, and also by

<sup>1)</sup> Berl. Berichte **38** (1905), 3796.

<sup>2)</sup> Berl. Berichte **35** (1902), 2519 and 3695.

<sup>3)</sup> Compt. rend. **126** 1898), 525.

Letts<sup>1)</sup>, from pinene hydrochloride and sodium, and whose melting point the above-mentioned authors indicated as 75°, boiling point 326 to 327°.

Borneol is also formed, in a yield of about 20%, when magnesium is allowed to act on pinene hydrochloride. It is present, in addition to hydrodicamphene, in the ethereal layer of the reaction mass, and distils over in the first fractions. It was produced in the pure state by esterification of the corresponding fractions with phthalic acid anhydride. Borneol owes its origin clearly to the action of the oxygen of the air on hydropinene magnesium chloride, when in all probability borneolate is formed.

By the action of magnesium and carbon dioxide on bornyl chloride  $C_{10}H_{17}Cl$ , an acid of the melting point 72° is formed, bornyl carboxylic acid  $C_{10}H_{17}COOH$ , which is identical in every respect with hydropinene carboxylic acid.

### Alcohols.

When reducing carvacrol according to the method of Sabatier and Senderens<sup>2)</sup>, L. Brunel<sup>3)</sup> obtained two isomeric alcohols of the formula  $C_{10}H_{20}O$ . The compounds, designated as  $\alpha$ - and  $\beta$ -carvacromenthols, have the following properties:

$\alpha$ -Carvacromenthol is an oily, colourless liquid with the odour of safrol and thyme oil. The boiling point lies at 219°.

$\beta$ -Carvacromenthol could be purified by its phthalic acid compound, which could be recrystallised from alcohol; it is an oily, colourless liquid with a pleasant odour reminding of safrol and peppermint. Boiling point 222°;  $d_0$  0,918. Of this alcohol the following derivatives were produced; 1.  $\beta$ -carvacromenthyl formate, from formic acid and the alcohol; boiling point 229°  $d_0$  0,954. — 2.  $\beta$ -carvacromenthyl acetate, from acetic acid and the alcohol at 130°; boiling point 231,5°;  $d_0$  0,933. — 3. The acid succinic ester from succinic anhydride and the alcohol; melting point 74°. — 4. The acid phthalic ester from phthalic anhydride and the alcohol; melting point 136°.

Menthol. J. Kondakow<sup>4)</sup> enters into theoretical considerations on the subject of the five stereo-isomeric menthols hitherto known. He mentions first the ordinary l-menthol, whose properties and derivatives have hitherto been examined most in detail. It is well known that in the production of these derivatives, both stereo-

<sup>1)</sup> Berl. Berichte **13** (1880), 793.

<sup>2)</sup> Comp. Report October **1905**, 100—105.

<sup>3)</sup> Compt. rend. **141** (1905), 1245.

<sup>4)</sup> Journ. f. prakt. Chem. II. **72** (1905), 185.

chemical and chemical isomerisations occur, so that the final products no longer correspond to secondary, but to tertiary menthol. But in Kondakow's opinion, the assumption of an intermediary formation of d-menthol does not yet explain this fact satisfactorily. A more recent examination of d-menthol which Kondakow<sup>1)</sup> had produced by reduction from the ketone contained in oil of buchu leaves, has, namely, shown that this body, contrary to the opinion held up to the present, is not by any means unstable. Its haloid anhydrides are all dextrorotatory. In producing them, isomerisations take place — as in the case of l-menthol —, and there occur consequently stable, dextrorotatory, genuine derivatives of d-menthol, as well as unstable derivatives belonging to the tertiary menthol. Menthene, obtained from l-menthol, is dextrorotatory. Different from Kondakow's d-menthol is the isomenthol of Beckmann<sup>2)</sup>, which is formed jointly with d-menthol, when either l- or d-menthone is reduced.

Isomenthol is dextrorotatory, and differs from d-menthol by a higher melting point ( $83,5$  to  $84^\circ$ ) and a lower specific rotatory power ( $[\alpha]_D + 25,64^\circ$  to  $27,07^\circ$ ). On oxidation it is converted into d-menthone<sup>3)</sup>, which forms a dextrorotatory oxime. Although a more detailed examination of isomenthol and its derivatives is still wanting, it may be concluded, in view of its optical behaviour, that in respect of the stereochemical configuration of its molecule, it occupies an intermediary position between the two first menthols, with an approach towards d-menthol. Another l-isomenthol which would approximate more towards the l-antipode is not yet known, but can possibly be produced by means of reduction from iso-l-menthone. There are further known three inactive menthols. One of these was obtained by Kremers<sup>4)</sup> from optically inactive menthone. It melts at  $29$  to  $31^\circ$ , and may possibly be identical with the  $\beta$ -thymomenthol of the melting point  $27^\circ$  and boiling point  $217^\circ$  obtained by Brunel<sup>5)</sup> from thymol. The second was produced by Beckmann<sup>6)</sup>. Baer<sup>7)</sup> found a third liquid inactive menthol, which, however, according to its physical properties and chemical behaviour, stands closer to the terti-

<sup>1)</sup> Journ. f. prakt. Chemie II. **63** (1901), 49; Report April **1901**, 14.

<sup>2)</sup> Journ. f. prakt. Chemie II. **55** (1897), 14; Report April **1897**, 53.

<sup>3)</sup> According to tests by Skworzow, d-menthone ( $[\alpha]_D + 26,91^\circ$ ), when treated with ammonium formate, also yields formyl-d-menthylamine of the m. p.  $117$  to  $118^\circ$   $[\alpha]_D + 154,47^\circ$ , with little l-amine.

<sup>4)</sup> Amer. chem. Journ. **18** (1896) 762; Report October **1896**, 54.

<sup>5)</sup> Compt. rend. **140** (1905), 252; **137** (1903), 1268; Bull. Soc. Chim. III. **33** (1905), 269; **34** (1905), 500; **35** (1905), 569; Report April **1905**, 104; October **1905**, 103.

<sup>6)</sup> Journ. f. prakt. Chem. II. **55** (1897), 30; Report April **1897**, 53.

<sup>7)</sup> On the synthesis of an inactive menthene. Thesis, Leipzig **1898**; Report October **1898**, 56.

ary menthol which is now also produced by synthesis. With carbanil it forms no urethane, but loses readily thereby water, and yields an inactive menthene. Schindelmeiser has recently examined tertiary menthol more closely in Kondakow's laboratory, and has found that it behaves like Baer's alcohol. The menthene formed in the same manner has the following constants: boiling point  $170$  to  $175^\circ$ ;  $d_{\frac{20}{4}}^\circ$   $0,812$ ;  $n_{D20}^\circ$   $1,45627$ ;  $\alpha_D \pm 0^\circ$ . It forms a liquid nitrosochloride which passes over undecomposed with water vapour, which does not readily split off hydrochloric acid with sodium alcoholate or alcoholic potash, and consequently does not readily yield nitrosomenthene. The nitrosochloride boils at  $128$  to  $140^\circ$  ( $11$  mm. pressure), and is inactive. The solid nitrosochloride from Kremers' menthol cannot be driven over with water vapour without decomposition. Kondakow has obtained another inactive menthol, different from Baer's, when reducing diosphenol; boiling point  $214,5$  to  $216^\circ$  (atmospheric pressure),  $98$  to  $100,5^\circ$  ( $12$  mm. pressure),  $d_{20}^\circ$   $0,9052$ ,  $n_D$   $1,464456$ , molecular refraction  $47,59$ . It congeals on cooling, and with suitable treatment yields an inactive menthene of the following properties; boiling point  $168$  to  $169^\circ$ ,  $d_{\frac{19,80}{4}}^\circ$   $0,8264$ , molecular refraction  $45,73$ . This menthol greatly resembles Brunel's<sup>1)</sup>  $\alpha$ -thymomenthol, for which the following constants are given: boiling point  $215,5^\circ$ ;  $d_0^\circ$   $0,913$ ; melting point  $-5^\circ$ . The corresponding menthene boils at  $167$  to  $168^\circ$ ,  $d_{15}^\circ$   $0,823$ . But whether these two menthols are identical must remain for the present an open question.

With regard to the examination of the oil of buchu leaves, Kondakow states further that dipentene and limonene are present in it. The ketone to which reference has already been made, boils at  $86^\circ$  ( $10$  mm. pressure);  $\alpha_D - 51^\circ$ . It forms a liquid oxime and a hydrazone of the melting point  $80^\circ$ , further two semicarbazones with the melting points  $180$  and  $123^\circ$ . From the former is regenerated by means of sulphuric acid a strongly inverted ketone with the following physical constants: boiling point  $85,5$  to  $86^\circ$  ( $10$  mm. pressure),  $d_{19,5}^\circ$   $0,897$ ,  $[\alpha]_D - 22,3^\circ$ ,  $n_D$   $1,45169$ , molecular refraction  $46,28$ .

Tertiary menthol, and from it an inactive menthene, have been produced by W. H. Perkin jun.<sup>2)</sup> by synthesis in the following manner:  $\alpha$ -Bromohexahydro-p-toluylic acid, formed from hexahydro-p-toluylic acid on treatment with phosphorus pentachloride and bromine, yields on hydrolysis with dilute soda solution, in addition to  $\Delta_1$ -tetrahydro-p-toluylic acid,  $\alpha$ -hydroxyhexahydro-p-toluylic acid of the melting

<sup>1)</sup> Bull. Soc. Chim. III. **33** (1905), 569; Report April 1905, 103.

<sup>2)</sup> Proceed. Chem. Soc. **21** (1905), 255.

point  $132^{\circ}$ . The last-named acid is readily converted under the action of dilute sulphuric acid into 1,4-methycyclohexanone of the boiling point  $170^{\circ}$ . The reaction takes place with elimination of carbonic oxide. At the same time, considerable quantities of  $\Delta_1$ -tetrahydro-p-toluylic acid are formed. With magnesium isopropyl iodide the ketone forms tertiary menthol of the boiling point  $95^{\circ}$  (25 mm. pressure). The alcohol, when heated with potassium bisulphate, splits off water, and is converted into inactive menthene of the boiling point  $168^{\circ}$ . The nitrosochloride of this menthene is solid, and like that of the menthene obtained by Kremers and Urban<sup>1)</sup>, melts at  $128^{\circ}$ .

Sesquiterpene alcohols. Eyken<sup>2)</sup> reports on the occurrence of sesquiterpene alcohols in the distillates of a few aromatic woods of the Malay Archipelago.

Some considerable time ago van Romburgh had obtained by steam distillation from the "Kajoe garoe" (fragrant wood) of Macassar, whose botanical origin was unknown, an oil interspersed with solid crystals, which Eyken examined more closely. By expressing and purifying the crystals, they were recognised by their melting point  $93^{\circ}$ , by analysis, optical rotation  $[\alpha]_D - 30^{\circ}$ , and molecular refraction, as guaiol; a comparison with guaiol from guaiac wood oil confirmed the identity. In the liquid portions of the oil free acids were found, chiefly formic and acetic acids. Subsequently Eyken himself produced the oil by distilling the wood; the latter he suspected to be a conifer, possibly a species of juniper. He obtained the oil in a yield of 1.3%; it soon became solid, but, contrary to the oil first examined, it contained no fractions passing over below the boiling point of guaiol; the fractions boiling higher than guaiol remained also liquid, and thereby rendered it more difficult to work out the latter, which should therefore be obtained not by fractionating, but by freezing out. In spite of the differences Eyken considers the two oils to be identical, and attributed the variations to this, that the one oil had been stored for several years, the other one being a fresh distillate.

The same author obtained a sesquiterpene alcohol differing from those known up to the present, in the course of an examination of the oil of *Gonostylus Miquelianus* T. et B., the wood of which also has the name "Kajoe garoe". This oil was also solid, and melted towards  $66^{\circ}$  to  $68^{\circ}$ ; boiling point  $280^{\circ}$  to  $290^{\circ}$ ;  $[\alpha]_D$  in absolute alcohol  $+35^{\circ}$ . In order to remove resins, the oil in ethereal solution was washed with potash liquor, and after evaporating the ether, distilled twice. When

<sup>1)</sup> Amer. chem. Journ. **16** (1894), 385; Report April 1894, 72.

<sup>2)</sup> Recueil des trav. chim. des P.-B. **25** (1906), 40, 44. Chem. Centralbl. **1906**, I, 841.

distilled with water vapour, however, the colourless oil decomposed, and yielded a distillate with an acid reaction and a solid resin-like residue. For this reason, the solid body of this oil must be obtained by freezing out; after recrystallisation from acetic acid and from alcohol it showed the following constants: formula  $C_{25}H_{26}O$ , melting point  $82^{\circ}$ ; boiling point  $164$  to  $166^{\circ}$  (17 mm. pressure), molecular weight calculated 222, found 232, 228,  $[\alpha]_D$  in absolute alcohol  $+30^{\circ}$ . Eyken gives it the name "gonostylol". When boiled with formic acid the alcohol was converted into a sesquiterpene  $C_{15}H_{24}$ , gonostylene, of the boiling point  $137^{\circ}$  to  $139^{\circ}$  (17 mm.)  $d_{17} 0.9183$ ,  $[\alpha]_D$  in absolute alcohol  $+40^{\circ}$ , molecular refraction found 66.7 calculated for  $C_{15}H_{24}O$  66.15. It is remarkable that guaialol and guaiane have the same rotatory power, but in the reverse direction. With hydrochloric acid and with bromine respectively only oily products of addition were obtained. When treated with glacial acetic and sulphuric acids according to Bertram-Walbaum, no alcohol was formed; the bulk of the terpene remained unchanged.

### Aldehydes and ketones.

We have already repeatedly discussed in our Reports the method for the determination of aldehydes and ketones with neutral solution of sodium sulphite, recommended by Sadtler<sup>1</sup>), and have in every case been compelled to question the accuracy of this method, as an exact titration of the solution containing sodium sulphite is not possible. Further studies of his method have shown Sadtler<sup>2</sup>) that he was in error with regard to the increase in the application of his method. The author determined again the usefulness of the method for citral, cinnamic aldehyde, benzaldehyde, vanillin, carvone, pulegone, formaldehyde, citronellal, camphor, menthone and fenchone. Of these compounds, citral, cinnamic aldehyde, carvone, pulegone, and formaldehyde reacted with 2 molecules sodium sulphite; benzaldehyde and vanillin with 1 molecule sodium sulphite, and the others not at all.

In almost every case Sadtler now lets the liquid with oil and neutral sulphite stand overnight, in order to be sure that no further alkali is formed. Previous to adding the sulphite solution, the oils are neutralised with  $\frac{1}{10}$ th normal alkali solution. Sadtler has recently stated that the disappearance of the characteristic odour (especially in citral, cinnamic aldehyde, carvone, pulegone, and benzaldehyde) is an important sign of the end of the reaction.

<sup>1</sup>) Report April 1904, 48; October 1904, 119; April 1905, 103; October 1905, 30.

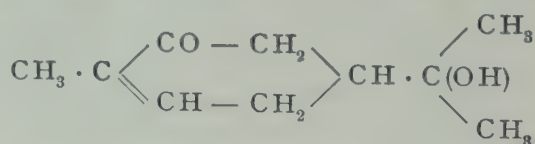
<sup>2</sup>) According to reprint from the Journ. Americ. Chem. Soc. 27 (1905), 1321.

The author concludes from the results obtained, that the presence of double linkings and their situation towards the CHO- or CO-group, and also of the benzene nucleus and its situation, have an influence on the reaction between neutral sodium sulphite and aldehydes and ketones. As formaldehyde reacts so very readily, the reaction appears to occur all the more easily, the smaller the molecular weight is of the body which enters into reaction. In Sadtler's opinion the CHO-group specially appears to become active in this reaction, and not the double linking, as Tiemann believes. Salicylic aldehyde, anisic aldehyde, cuminic aldehyde and heliotropin also appear, like benzaldehyde, to react only with 1 molecule neutral sodium sulphite.

After experiments<sup>1)</sup> which we have recently made again, we are unable to alter anything in our previously expressed opinion on Sadtler's method; its usefulness for exact determinations fails on account of the impossibility of titrating the sodium sulphite solution exactly.

Benzaldehyde. With regard to the determination of small quantities of benzaldehyde according to Hérissé, see page 107 of the present Report.

Carvone. Knoevenagel and Samel<sup>2)</sup> have obtained in a round-about way the oxydihydrocarvone produced by Rupe and Schlochoff<sup>3)</sup>, by bringing carvone in solution by boiling with alkali-bisulphite liquor, and letting this solution stand together with strong acids at ordinary temperature. In supersaturating with soda liquor, 80% of the carvone were then separated off as carvone hydrate (as the authors call this body). It is formed, as in the case of Rupe and Schlochoff's method, by attaching water to the double linking of the side-chain of carvone. Carvone hydrate



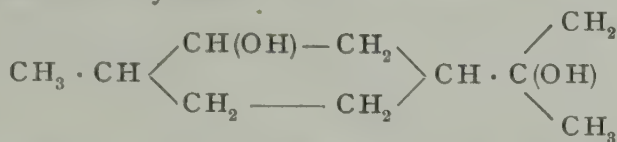
has the following properties: boiling point 160° at 16 mm. pressure; melting point 42 to 43° (from ligroin and petroleum ether),  $[\alpha]_{\text{D}20} +43^\circ$  in 25,85 per cent. alcoholic solution. It is insoluble in water (according to Rupe and Schlochoff it is readily soluble); phenylhydrazone, melting point 134 to 135°; oxime, 112,5 to 114°; semicarbazone, 177°.

<sup>1)</sup> Compare the present Report, p. 70 and 74.

<sup>2)</sup> Berl. Berichte **39** (1906), 677.

<sup>3)</sup> Berl. Berichte **38** (1905), 1719. Report October 1905, 112.

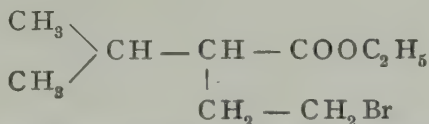
to 179°. When heated *in vacuo* for a prolonged time, carvone hydrate is converted in carvacrol and carvone; when heated for one hour with potassium bisulphate to 170°, it yields quantitatively carvacrol. The hydroxyl-group could not be detected either with benzoyl chloride or with phenyl isothiocyanate; all efforts to condense carvone hydrate with benzaldehyde also failed. Reduction with sodium and alcohol led to dihydrocarveol hydrate



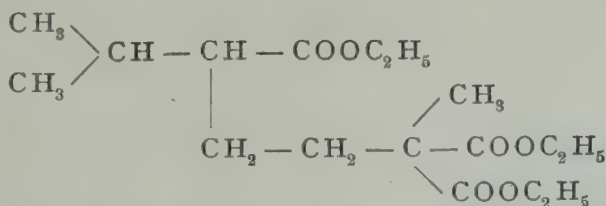
melting point 112°;  $[\alpha]_{\text{D}20^\circ} + 19,2^\circ$  in 24,74 per cent. alcoholic solution. Reduction with zinc dust and potash liquor, carried out in a manner analogous to the reduction of carvone to dihydrocarvone, yielded dihydrocarvone hydrate of the boiling point 138 to 139° (9 mm. pressure);  $d_{40}^{19^\circ} 1,006$ ;  $n_{\text{D}20^\circ} 1,476$ ;  $[\alpha]_{\text{D}20^\circ} - 18,5^\circ$  in 18,48 per cent. alcoholic solution; semicarbazone melting point 150,5° to 151°. Dihydrocarveol hydrate could be oxidised with chromic acid and glacial acetic acid to dihydrocarvone hydrate.

Camphor. Dihydrocamphoric acid, formed when camphoric acid and potash are melted together, is, according to Martine,  $\alpha$ -methyl- $\alpha$ -isopropyladipic acid, which is also obtained on oxidation of benzylidene menthone. In order to confirm this formula, G. Blanc<sup>1)</sup> has made an attempt to arrive at this acid by synthesis.

He reduced for this purpose isopropylsuccinic acid, according to a method<sup>2)</sup> already described previously, with sodium in absolute alcohol. The  $\alpha$ - and  $\beta$ -isopropyl-butylolactones were treated with phosphorus pentabromide and subsequently with alcohol. Thereby is formed the ester



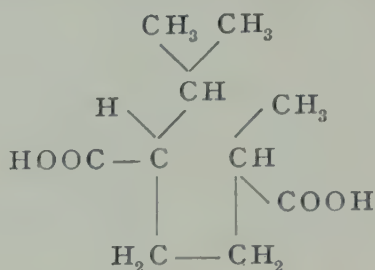
which is converted with sodium methyl malonic acid ester, with formation of



<sup>1)</sup> Compt. rend. 141 (1905), 1030.

<sup>2)</sup> Compt. rend. 139 (1904), 203.

This ester yields on saponification an acid melting at  $158^{\circ}$ , which on being melted splits off carbonic acid, and is converted into  $\alpha$ -methyl- $\alpha$ -isopropyladipic acid:

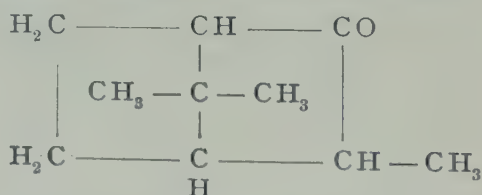


It melts at  $103^{\circ}$ , and corresponds to dihydrocamphoric acid. But the latter is optically active, whilst the synthetic acid is inactive.

In continuation of a work on the electrolytic reduction of the imide of camphoric acid<sup>1)</sup> which has led to the formation of the so-called camphidones and of camphidine, J. Tafel and H. Bublitz<sup>2)</sup> publish the result of their investigations which deal with the elucidation of the constitution of these reduction products.

Camphocarbonic acid, as is well known, splits up, when heated, into carbon dioxide, and camphor. W. Balcom<sup>3)</sup> has investigated the physical progress of this reaction. We content ourselves with a reference to this work.

Fenchone. On the strength of recent investigations, F. W. Semmler<sup>4)</sup> has convinced himself that the formula



drawn up by Wallach<sup>5)</sup> for fenchone, and up to the present recognised as correct, does not agree with all the facts. If it is accepted with Kondakow, that in the formation of fenchyl chloride from fenchyl alcohol a transposition takes place into the tertiary fenchyl chloride, in which the chlorine atom and the methyl-group are linked

<sup>1)</sup> Berl. Berichte **34** (1901), 3274.

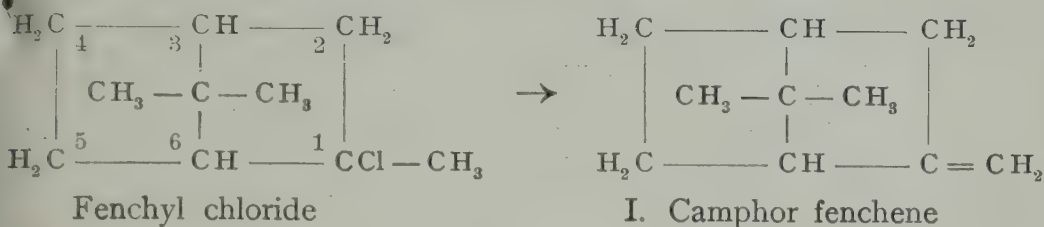
<sup>2)</sup> Berl. Berichte **38** (1905), 3806.

<sup>3)</sup> The chemical kinetics of the loss of carbon dioxide from camphocarbonic acid. Thesis, Heidelberg, **1905**.

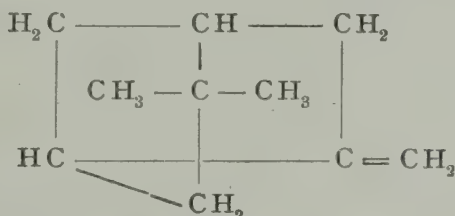
<sup>4)</sup> Chem. Ztg. **29** (1905), 1313.

<sup>5)</sup> Liebig's Annalen **300** (1898), 319.

to the same carbon-atom, there may originate, with loss of hydrochloric acid, on the one hand a fenchene of the formula I, "camphor fenchene", but on the other hand there might be formed with ring-disruption between the carbon atoms 1 and 6, a fenchene of the formula II, "isofenchone fenchene": —

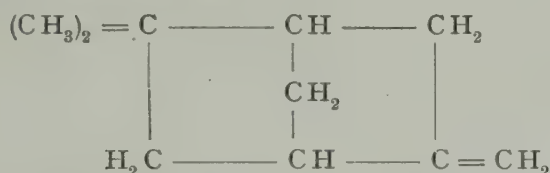


and

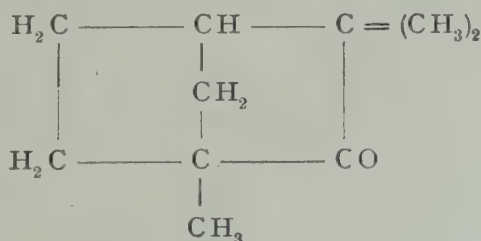


II. Isofenchone fenchene

Formula II is identical with



It this is accepted, the formation of the two semi-cyclic fenchenes from Wallach's fenchone formula could be explained. But according to more recent investigations by Semmler, this hypothesis cannot be sustained without further proof. Particularly by the results of the oxidation in alkaline and neutral solutions, which led from fenchone to isocamphoronic acid and dimethyl tricarballic acid, Semmler was induced to draw up the following formula for fenchone: —

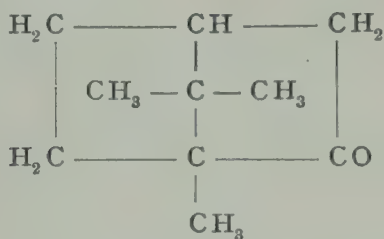


The formation of the two acids could be explained from this formula without re-arrangement. Gardner and Cockburn<sup>1)</sup> also ob-

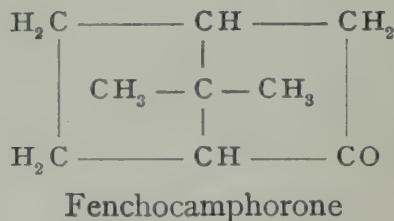
<sup>1)</sup> Journ. Chem. Soc. **73** (1898), 708.

tained the above acids from fenchone, but with concentrated nitric acid, whilst Wallach had had already before him dimethyl malonic acid, formed by further oxidation of dimethyl tricarballic acid. The conversion of fenchone into m-cymene, discovered by Wallach, would also be intelligible in accordance with Semmler's fenchone formula; similarly, the relationship existing between camphor and fenchone, and also the various well-known reactions of fenchone and its derivatives, would find a better explanation by the new formula. In agreement with the new formula are further the physical properties of fenchone, and this is particularly evident if the properties of camphor and fenchone are contrasted.

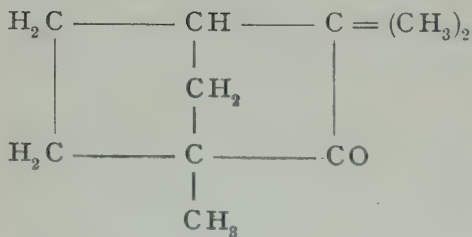
According to this, camphor and fenchocamphorone on the one side, and fenchone and camphenilone on the other, go together.



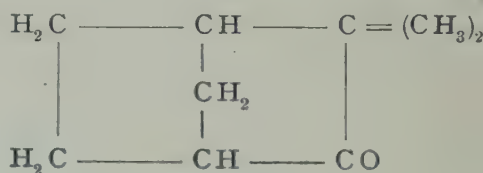
Camphor



Fenchocamphorone



Fenchone



Camphenilone

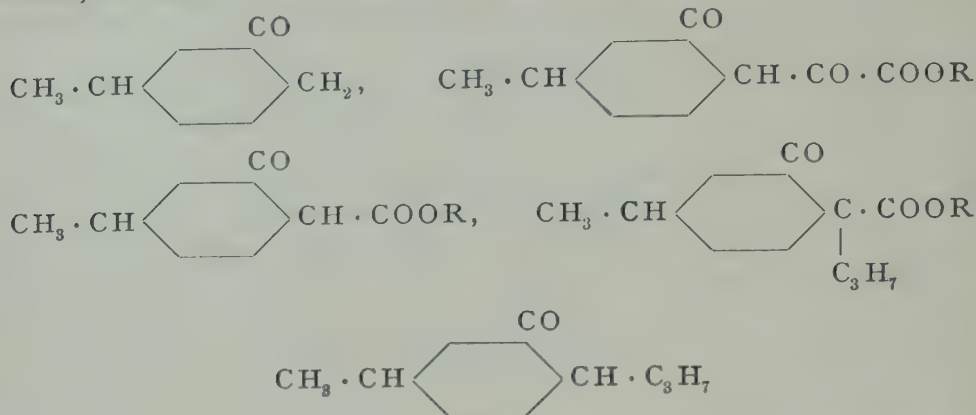
Camphor would consequently be methylated fenchocamphorone, and fenchone methylated camphenilone.

Menthone. A. Kötz and L. Hesse<sup>1)</sup> report on a synthesis of menthone from methylhexanone. They condense methylhexanone and ethyl oxalate by adding a strongly cooled mixture of ester and ketone in small portions to a solution of sodium ethylate which is kept cold. The temperature may thereby rise only slightly and temporarily above that of the freezing mixture. After standing for 15 hours, the dark-brown reaction mixture is introduced into very dilute sulphuric acid of 0°; the oxalic ester of methylhexanone formed

<sup>1)</sup> Liebig's Annalen 342 (1905), 306.

is abstracted from the aqueous liquid by repeatedly extracting with ether. It is clear from the following results of this work that the oxalic acid ester enters the methylhexanone in para-position towards the methyl-group, and that consequently methyl-1-hexanone-3-oxalic ester-4 has been formed. The condensation-product gives a dark-brown coloration in alcoholic solution with ferric chloride. Concentrated soda liquor splits up the ester into methyl hexanone and sodium oxalate. With ammonia it also reproduces the ketone and oxamide. The crude condensation product yields with copper acetate a bright green copper salt, which melts at  $153^{\circ}$ . The pure ester separated from the copper salt by dilute sulphuric acid boils at  $163^{\circ}$  (12 to 13 mm. pressure);  $d_{15^{\circ}} 1,0903$ . Its semicarbazone melts above  $245^{\circ}$ . Dilute sulphuric acid or soda liquor saponify it readily into methylhexanone oxalic acid which melts at  $132^{\circ}$ . When heated with aniline in a water bath, the ester forms a pyrrolidone derivative of the formula  $C_{21}H_{20}ON_2$ . When distilled at atmospheric pressure, it is converted with loss of carbonic oxide into methyl-1-hexanone-3-carboxylic ester-4, a mobile liquid of the boiling point  $128,5^{\circ}$  (15 mm. pressure);  $d_{14^{\circ}} 1,057$ . Its copper salt melts at  $155^{\circ}$ . With phenylhydrazine the ester yields a pyrazolone of the melting point  $243^{\circ}$  to  $245^{\circ}$ ; with ammonia tetrahydromethyl anthranilic acid ester of the melting point  $67^{\circ}$ . The corresponding methyl ester stands, according to the odour, in no relation whatever to methyl ester of methyl anthranilic acid. With suitable treatment with methyl iodide and a solution of sodium in methyl alcohol, methylhexanone carboxylic ester is converted into methyl-1-hexanone-3-methyl-4-carboxylic ester-4. The specific gravity of the ester boiling at  $120^{\circ}$  to  $122^{\circ}$  (12 mm. pressure) is 1,0189 ( $19^{\circ}$ ). The isopropyl ester constituted in an analogous manner boils at  $135^{\circ}$  to  $137^{\circ}$  (10 mm. pressure);  $d_{14^{\circ}} = 1,009$ . Its semicarbazone melts at  $144^{\circ}$  to  $145^{\circ}$ . When splitting up the ketone with concentrated methylalcoholic potash there is formed the natural d-menthone of the boiling point  $206^{\circ}$  to  $208^{\circ}$ ;  $d_{18^{\circ}} 0,898$ ;  $[\alpha]_D + 11,68^{\circ}$ ; the corresponding semicarbazone melts at  $184$  to  $185^{\circ}$ . As in this case the specific rotatory power ( $[\alpha]_D + 28,14^{\circ}$ ) is only about half as large as that of the d-menthone which can be obtained from natural l-menthone by inversion with concentrated sulphuric acid, it may be assumed that in the case before us, lævorotatory menthone is present in addition to a preponderance of dextrorotatory menthone. On reduction with sodium and alcohol, only lævorotatory menthone is formed, of which one fraction boils at  $214^{\circ}$  to  $216^{\circ}$ , and congeals into crystals melting at  $37^{\circ}$ . The other fraction of the boiling point  $212^{\circ}$  to  $214^{\circ}$  can only be obtained crystallised by continued cooling. The urethanes of both menthols melt at  $111^{\circ}$ , like that of natural menthol. The formation of the ordinary para-menthone has proved that the above condensation product

and the bodies which can be derived from it possess the accepted formula, which finds expression in the following diagrams: —



Methylheptenone. In connection with a short theoretical contemplation of the base  $\text{C}_8\text{H}_{15}\text{N}$ <sup>1)</sup> which he had previously obtained from methyl heptenylamine and described, O. Wallach<sup>2)</sup> reports on a new base  $\text{C}_8\text{H}_{16}:\text{NH}$ , isomeric with coniine, which had been produced from the same crude material. It is formed, besides a hydrocarbon  $\text{C}_8\text{H}_{14}$ , by the addition of hydrogen chloride or hydrogen bromide to methylheptenyl amine, and subsequent dry distillation of the addition product. The base has the following properties: boiling point  $150$  to  $151^\circ$ ;  $d_{0,823}$ ;  $n_{D20} 1,4398$ ; melting point of the hydrochloride  $218$  to  $220^\circ$ , of the chloroplatinate  $221$  to  $233^\circ$ . It yields a quaternary iodide of the composition  $\text{C}_8\text{H}_{16}\text{N}(\text{CH}_3)_2\text{I}$  (melting point  $242$  to  $243^\circ$ ), a nitroso compound and a sulphone amide of the melting point  $76$  to  $78^\circ$ . The constitutional formula of the base is probably



Cyclohexanone. O. Wallach<sup>3)</sup> describes a series of derivatives of cyclohexanone of which the bromine substitution products have already been referred to in our last Report<sup>4)</sup>. The splitting up of cyclohexanone isoxime<sup>5)</sup> previously described in  $\epsilon$ -amido-n-caproic acid, could be confirmed by conversion of this acid into normal adipic acid. The reduction of the isoxime with sodium and amyl alcohol led, in addition to acids formed by splitting up the isoxime, to a mixture of bases, from which cyclohexylamine  $\text{C}_6\text{H}_{11}\text{NH}_2$  (boiling

<sup>1)</sup> Liebig's Annalen **319** (1901), 104. Report April 1902, 92.

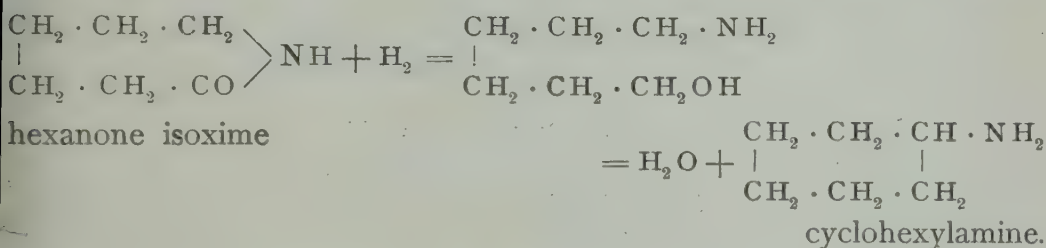
<sup>2)</sup> Berl. Berichte **38** (1905), 2803.

<sup>3)</sup> Liebig's Annalen **343** (1905), 40.

<sup>4)</sup> Report October 1905, 108.

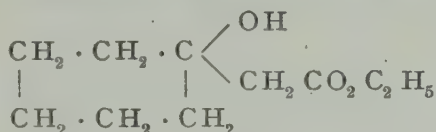
<sup>5)</sup> Liebig's Annalen **312** (1900), 187. Report October 1900, 74.

point 134 to 138°;  $d_{0,863}$ ;  $n_{D24}$  1,4575; melting point of the hydrochloride 203 to 204°, of the benzoyl compound 149°, the urea 195 to 196°) could be separated off. The hexamethylenimine which might be expected could not be isolated. As only pure isoxime free from oxime was used, the occurrence of cyclohexylamine can only be explained by ring-disruption and new ring-formation in the following manner: —



Wallach mentions further the conditions under which the nitrosochloride of cyclohexene (tetrahydrobenzene) which had already been obtained in small quantity by Baeyer, is produced in a better yield. It has not yet been possible to convert this nitrosochloride in the still unknown oxime of hexenone.

In an analogous manner to methyl cyclohexanone<sup>1)</sup>, Wallach obtained by the action of bromoacetic ester on cyclohexanone in the presence of zinc or magnesium, cyclohexanol acetic ester: —



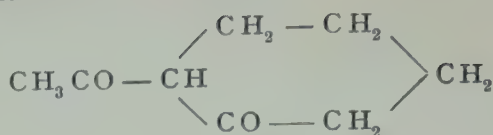
This body is converted by loss of water into cyclohexene acetic ester, and the latter by saponification into cyclohexene acetic acid, which melts at 37 to 38°, and boils at 140° at 12 mm. pressure. By adding bromine it yields a brominated acid (melting point 119 to 120°), and on oxidation with potassium permanganate in a weak alkaline solution, an oil with a hexanone-like odour, whose semicarbazone melts at 203 to 204°. The analysis points to a compound with seven carbon atoms, which, however, possesses the character of an aldehyde.

Acetylcyclohexanone. George Leser<sup>2)</sup> has obtained by condensation of cyclohexanone and acetic ester by means of sodium, in a fairly good yield, acetylcyclohexanone, a liquid with a penetrating odour, which boils at 111 to 112° at 18 mm. pressure;  $d_{0,10782}$ ;  $n_D$  1,51384.

<sup>1)</sup> Liebigs Annalen **314** (1900), 151. Report April 1901, 61.

<sup>2)</sup> Compt. rend. **141** (1905), 1032.

# Acetylcyclohexanone

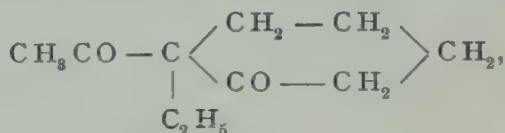


forms a monosemicarbazone of the melting point  $159^\circ$ , and a dioxim. It dissolves readily in alkalies. When the alkaline solution is heated a complete hydrolytic decomposition occurs, and if hydrochloric acid is added, acetylcaproic acid separates off: —



This boils at  $184$  to  $185^\circ$  at  $15$  mm. pressure, and congeals into mass melting at  $30^\circ$ . On oxidation with bromine and soda liquor it is converted into normal pimelic acid of the melting point  $103^\circ$ .

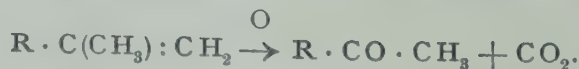
Acetylcyclohexanone has a mobile hydrogen atom which can be replaced by radicals. Leser for example obtained the ethyl derivative



which, however, no longer shows the characteristic properties of the  $\beta$ -diketones. The study of these derivatives is continued.

## Phenols and phenol ethers.

Béhal and Tiffeneau<sup>1)</sup> have continued their earlier investigations of phenol ethers with  $\psi$ -allyl side-chain  $-\text{C}(\text{CH}_3):\text{CH}_2$ , and, starting from the three o-, m-, and p-substituted  $\psi$ -anethols,  $\psi$ -allyl-p-phenetol,  $\psi$ -safrol, and  $\psi$ -methyleugenol, they have arrived at the following results. On reduction with sodium and alcohol, the  $\psi$ -allyl group is reduced to isopropyl; thus, in the case of isopropylphenetol, the  $\text{OC}_2\text{H}_5$ -group was eliminated by hydriodic acid, and the free phenol identified by its melting point and that of its benzoate. If the  $\psi$ -allyl bodies are oxidised with aqueous chameleon solution in the cold, the ketones are formed, with loss of  $\text{CO}_2$ , substituted acetophenones: —

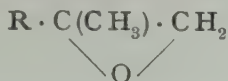


When hypiodous acid is added, iodohydrins  $\text{R} \cdot \text{C}(\text{OH})(\text{CH}_2 \cdot \text{CH}_2\text{I})$  are formed, which behave differently when hydriodic acid is added, according to the reagent employed. If they are treated<sup>2)</sup>

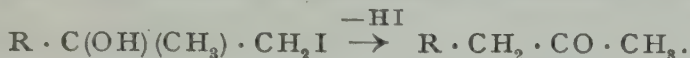
<sup>1)</sup> Compt. rend. **141** (1905), 596.

<sup>2)</sup> Compt. rend. **139** (1905), 139.

ethereal solution with potash powder, there are formed intermediately, by substitution of the iodine atom by OH and loss of water, oxides



which on distillation at atmospheric pressure converted into are hydratropic aldehydes  $\text{R} \cdot \text{CH}(\text{CH}_3) \cdot \text{CHO}$ . But if the hydriodic acid is split off with silver nitrate or mercuric oxide, there occurs, as already previously observed, a very remarkable migration of the carbon linkings, with formation of  $\beta$ -ketones, that is to say, formation of a normal side-chain:

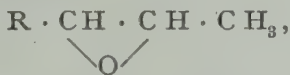


In this manner were produced from  $\psi$ -anethol  $\beta$ -anise ketone, from  $\psi$ -allyl phenetol  $p$ -ethoxy phenyl acetone, from  $\psi$ -safrol methylene dioxyphenyl acetone, and from  $\psi$ -methyl eugenol dimethoxyphenyl acetone, and the two last-named were identified by means of the semicarbazones with the products obtained in another way by Wallach and by Hoering.

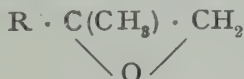
According to Fourneau and Tiffeneau<sup>1)</sup> substituted ethylene oxides of the benzene series behave differently, according to the position of the substitute when they are rearranged by the application of heat. The authors differentiate between monosubstituted oxides



symmetrically disubstituted

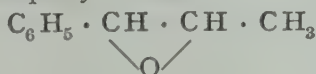


and asymmetrically disubstituted oxides



The first-named oxides, such as the oxides derived from allyl-benzene, estragol, safrol, and methyl eugenol, which pass over without decomposition at reduced pressure, are converted by distillation at ordinary pressure in substituted hydrocinnamic aldehydes,  $\text{R} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$ , which were identified by the melting points of their semicarbazones.

The symmetrically disubstituted oxides are converted into  $\beta$ -ketones of the formula  $\text{R} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$ ; there was, for instance, obtained from phenyl propenyl oxide



<sup>1)</sup> Compt. rend. **141** (1905), 662. Comp. ibid. **140** (1905), 545. Report October **1905**, 118.

phenyl acetone (boiling point  $214-215^{\circ}$ , melting point of the semicarbazone  $198^{\circ}$ ); in an analogous manner from anethol oxide, the anethol ketone (Tardy's anise ketone) obtained also by Hoering<sup>1</sup>).

The asymmetrically disubstituted oxides, as will be seen from the above report, are converted into substituted hydratropic aldehydes, which had already been produced by Bougault<sup>2</sup>) in an entirely different manner.

In all these conversions, there occur no molecular migrations (transposition of carbon linkings).

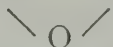
In our Report of October **1904**, 11, we communicated the results of a work by Hoering, according to which, in the treatment of monobromo anethol bromide  $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_3$  with nitric acid, the bromine atom of the side-chain in the  $\alpha$ -position enters the benzene ring, with formation of a ketone  $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH}_3$ . This peculiar atomic transposition was recently also observed by Hoering in the anethol dibromide itself, when even with moderate oxidation with nitric, chromic, or glacial acetic acid, a ketone  $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH}_3$  is formed in a good yield. An examination of the secondary products formed shows that there also occur secondary products non-brominated in the nucleus; on the other hand, when the latter are oxidised, higher brominated products are formed, *e. g.*, dibromo anisic acid. In order to solve the problem whether this entrance of bromine in the nucleus must not be attributed to the occurrence of free bromine, numerous oxidation experiments were made, especially with dilute solution of potassium permanganate. But as, in spite of every precaution, this examination did not lead to any definite result, Hoering endeavoured to come to a decision in an indirect way, by oxidising  $\alpha$ -methoxy- $\beta$ -bromo-dihydrobromo anethol  $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH}(\text{OCH}_3) \cdot \text{CHBr} \cdot \text{CH}_3$ . He found that with moderate oxidation of this body, no further bromine atom enters the benzene ring, as almost exclusively the ketone  $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH}_3$  was formed.

On oxidising isosafrol dibromide, the author did not succeed in arriving at a separation of the secondary products; on the other hand, when the dibromide was treated with a mixture of nitric and glacial acetic acids, it was converted into an acetyl derivative  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_2(\text{NO}_2) \cdot \text{CH}(\text{OCOCH}_3) \cdot \text{CHBr} \cdot \text{CH}_3$ , nitrated in the nucleus,

<sup>1</sup>) Berl. Berichte **38** (1905), 2296. Report October **1905**, 117; compare also the following abstracts.

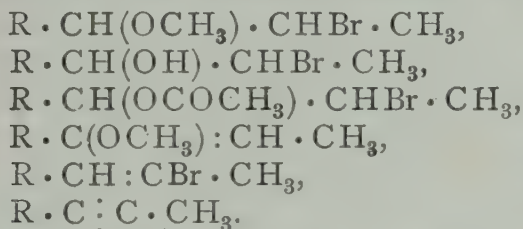
<sup>2</sup>) Annal. de Chim. et Phys. VII. **25** (1902), 515, 549, 560. Report April **1903**, 11.

which with alcoholic potash yielded a propylene oxide  $R \cdot \text{CH} - \text{CH} \cdot$



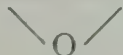
$\text{CH}_3$ . This conversion established the position of the two bromine atoms in the side-chain, and confirmed the accuracy of the pseudo-formula accepted by Hoering for the reactive dibromides.

The facility with which the bromine atom in the  $\alpha$ -position of the dibromides of propenyl phenol ethers is exchanged, was followed up some time ago by Pond<sup>1)</sup> and Hell<sup>2)</sup>. Hoering<sup>3)</sup> has again investigated this reactivity in anethol, isosafrol, and the corresponding derivatives brominated in the nucleus, in order to determine whether the entry of bromine in the benzene nucleus influences the mobility of the bromine atom in  $\alpha$ -position of the side chain. He thereby found that as a rule these dibromides brominated in the nucleus, if the reaction lasts sufficiently long, lead to the analogous bodies as the dibromides themselves. There were produced in the usual manner substitution and also addition products of the general form



In the same measure as the reactivity of the  $\alpha$ -bromine atom diminishes with the entry of bromine in the benzene nucleus, the capacity of the  $\beta$ -bromine atom of splitting off decreases. The  $\beta$ -bromine atom in the acetates  $R \cdot \text{CH}(\text{OCOCH}_3) \cdot \text{CHBr} \cdot \text{CH}_3$ , for instance, can only be replaced by acetoxyl with formation of monoacetates  $R \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OCOCH}_3) \cdot \text{CH}_3$ .

The compounds  $R \cdot \text{CH}(\text{OH}) \cdot \text{CHBr} \cdot \text{CH}_3$  and  $R \cdot \text{CH}(\text{OCOCH}_3) \cdot \text{CHBr} \cdot \text{CH}_3$ , which are derived from the dibromides, are, as Hoering published in a preliminary communication<sup>4)</sup>, very readily converted, by boiling with alcoholic potash, in substituted propenyl oxides of the formula  $R \cdot \text{CH} - \text{CH} \cdot \text{CH}_3$ . In a more detailed publication<sup>5)</sup>



Hoering has continued the study of these oxides, preferably with the oxides derived from mono- and dibromoisosafrol dibromides, as these were suitable for the purpose on account of their crystallisation capacity.

<sup>1)</sup> Journ. Amer. chem. Soc. **25** (1905), 292. Report October **1903**, 98.

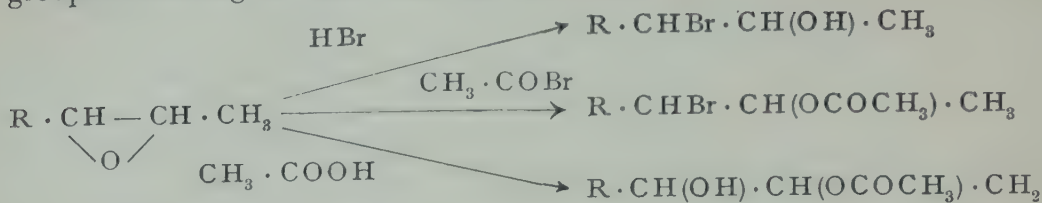
<sup>2)</sup> Berl. Berichte **36** (1903), 1184. Report October **1903**, 98.

<sup>3)</sup> Berl. Berichte **38** (1905), 3464.

<sup>4)</sup> Berl. Berichte **38** (1905), 2296. Report October **1905**, 117.

<sup>5)</sup> Berl. Berichte **38** (1905), 3477.

Like the ethylene oxides, these oxides also readily attach atom-groups according to the following formulæ:

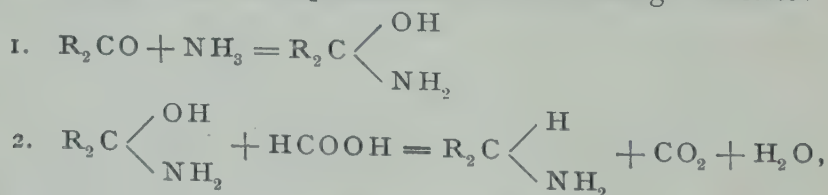


The oxide oxygen atom therefore always remains linked to the  $\beta$ -carbon atom, as is also the case in converting the oxides by heating or treatment with acids into  $\beta$ -ketones  $\text{R} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$ . The bromine atom of the side-chain in the  $\alpha$ -position, in the addition products of the oxides, is, as might be expected, very mobile; in fact in the  $\alpha$ -bromo- $\beta$ -oxy compounds so much so, that they decompose with evolution of hydrogen bromide.

With regard to the very rich experimental matter of these works, we must refer to the original treatises.

### Nitrogenous bodies.

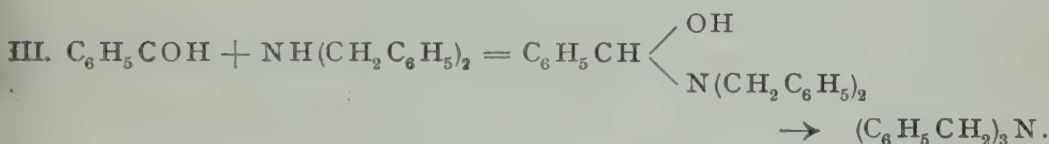
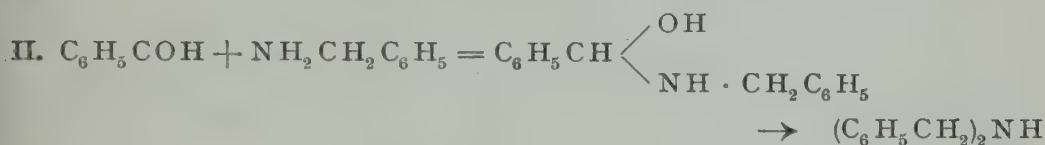
The conversion of aldehydes and ketones into bases by boiling with ammonium formate, has first been accomplished by Leuckart. He obtained the formyl compounds of the primary, secondary and tertiary bases corresponding to the crude material. O. Wallach has applied this reaction already a long time ago to terpene ketones. The occurrence of the mixture of bases and of the formyl compounds as final products complicated the production of the bases in the pure state, and for this reason Wallach<sup>1)</sup> set himself the task of removing this defect in the reaction. If the formyl compounds were only formed as secondary products from a primarily formed base and formic acid, a lowering of the temperature should prevent the formation of these compounds. This has in many cases proved to be feasible, and has at the same time identified the formyl compounds as secondary products of the reaction. The progress of the reaction could now be explained as is expressed in the following formulæ: —



in which formic acid represents the reducing agent. If then the primary base has an opportunity of entering in reaction with a still

<sup>1)</sup> Liebig's Annalen **343** (1905), 54.

unchanged ketone or aldehyde, it will be possible that, besides primary, secondary and even tertiary bases are also formed, as the following example with benzaldehyde shows: —



This explains Leuckart's observations. Wallach further argues that if the base is withdrawn from the reaction-mixture by adding a suitable free acid, the uniform progress of the reaction will be promoted, inasmuch as only primary, or (when salts of the primary base are sufficiently dissociated at the existing temperature) only secondary, or further also only tertiary base will be formed. The hypothesis of the progress of the reaction further permits of the possibility of bringing besides ammonia, substituted primary or secondary bases in the presence of free formic acid so into reaction with aldehydes and ketones, that new substituted bases are formed. The experiment has confirmed the hypothesis, and has given the following results: —

1. The reaction can be accomplished practically uniformly by adding free anhydrous formic acid or acetic acid.

2. It is possible to keep the temperature of the conversion mostly fairly low, and as a consequence the final products obtained are mainly the salts of the bases formed. Only in a few cases, especially with aromatic bases and with menthone, the occurrence of the formyl compound cannot be prevented.

3. The sphere of application is very large owing to the fact that different aldehydes and ketones can be brought into reaction with different bases.

In the experimental part of Wallach's work, a number of such bases produced by the above-mentioned reaction are described: —

Diethylcarbinamine  $(\text{C}_2\text{H}_5)_2\text{CH} \cdot \text{NH}_2$  from diethyl ketone, ammonium formate, and acetic acid at  $165^\circ$ ; boiling point  $90^\circ$ .

$\alpha$ -Phenylethylamine  $\text{C}_6\text{H}_5\text{CH}(\text{NH}_2)\text{CH}_3$  from acetophenone, ammonium formate, and acetic acid, at  $155^\circ$ ; boiling point  $186^\circ$ ;

melting point of the hydrochloride  $160^{\circ}$ . The formyl compound is formed without adding acetic acid. Boiling point  $200^{\circ}$  at 14 mm. pressure.

Cyclodihexylamine  $\text{NH}(\text{C}_6\text{H}_{11})_2$  from cyclohexanone, ammonium formate, and acetic acid at  $120^{\circ}$  to  $130^{\circ}$ ; boiling point  $251$  to  $252^{\circ}$ ,  $d_{0,925}$ ;  $n_{\text{D}18^{\circ}} 1,4861$ ; nitrosamine, melting point  $105$  to  $106^{\circ}$ .

Benzylcyclohexylamine  $\text{NH} \begin{cases} \text{CH}_2\text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_{11} \end{cases}$  from cyclohexanone,

benzylamine, and formic acid, at  $150^{\circ}$ ; b. p.  $281$  to  $282^{\circ}$ .

Dicyclomethylhexylamine  $\text{NH}(\text{C}_6\text{H}_{10}\text{CH}_3)_2$  from methylhexanone, ammonium formate, and formic acid at  $120$  to  $130^{\circ}$ , boiling point  $134$  to  $135^{\circ}$  at 12 to 14 mm. pressure, at atmospheric pressure in a current of hydrogen  $273^{\circ}$ ;  $d_{0,8878}$ ;  $n_{\text{D}21^{\circ}} 1,4756$ .

The base is a mixture of stereo-isomeric compounds. The same mixture was also, in conformity with the theory, obtained from methylcyclohexanone, methylcyclohexylamine, and formic acid at  $150^{\circ}$ .

Amylmethylcyclohexylamine  $\text{NH} \begin{cases} \text{C}_5\text{H}_{11} \\ \text{C}_6\text{H}_{10} \cdot \text{CH}_3 \end{cases}$  from amyl-

amine, methylhexanone, and formic acid at  $150^{\circ}$ ; boiling point  $234^{\circ}$ .

Benzylmethylcyclohexylamine  $\text{NH} \begin{cases} \text{CH}_2\text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_{10} \cdot \text{CH}_3 \end{cases}$  from ben-

zylamine, methylhexanone, and formic acid at  $150^{\circ}$ ; boiling point  $165$  to  $170^{\circ}$  at 12 mm. pressure;  $d_{0,946}$ ;  $n_{\text{D}22^{\circ}} 1,5182$ . The same base was also obtained from benzaldehyde, methylcyclohexylamine formate and formic acid, at  $160^{\circ}$ .

Formylmenthylamine  $\text{C}_{10}\text{H}_{19}\text{NH} \cdot \text{CHO}$  from menthone, ammonium formate, and glacial acetic acid, at  $175$  to  $185^{\circ}$ . The temperature of conversion is so high in this case, that the formyl compound is formed from the formate produced primarily.

Triisoamylamine  $(\text{C}_5\text{H}_{11})_3\text{N}$  from valeric aldehyde, ammonium formate, and formic acid, at  $90$  to  $130^{\circ}$ ; boiling point  $265$  to  $270^{\circ}$ .

Tribenzylamine  $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{N}$ , from benzaldehyde, ammonium formate and formic acid at  $135^{\circ}$ ; melting point  $91^{\circ}$ .

Diamylaniline  $(\text{C}_5\text{H}_{11})_2\text{N} \cdot \text{C}_6\text{H}_5$  from valeric aldehyde, aniline formate, and formic acid at  $70$  to  $100^{\circ}$ , and then  $105$  to  $110^{\circ}$ ; boiling point  $264$  to  $265^{\circ}$ .

Methylamylaniline  $(\text{CH}_3)(\text{C}_5\text{H}_{11})\text{N} \cdot \text{C}_6\text{H}_5$  from valeric aldehyde, methyl aniline and formic acid at  $110^{\circ}$ .

Benzylaniline  $C_6H_5CH_2NH \cdot C_6H_5$  from benzaldehyde, aniline formate, and formic acid at  $120$  to  $125^\circ$ , melting point  $32^\circ$ . The reaction with formation of secondary products does not proceed quite evenly.

Ethylbenzylamine  $(C_2H_5)(CH_2C_6H_5) \cdot NH$  from benzaldehyde, ethylamine hydrochloride, sodium formate, and formic acid at  $150^\circ$ ; boiling point  $199^\circ$ . First of all the formyl compound was formed which could be saponified with hydrochloric acid.

Benzylpiperidine  $C_6H_5CH_2 \cdot N \cdot C_5H_{10}$  from piperidine, benzaldehyde, and formic acid at  $180^\circ$ ; boiling point  $248^\circ$ .

**Schimmel & Co.**

J. J. Weber, Leipzig.

SEMI-ANNUAL REPORT  
OF  
SCHIMMEL & Co.  
(FRITZSCHE BROTHERS)

MILTITZ

NEAR LEIPZIG

LONDON • NEW YORK.



OCTOBER 1907.

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## List of abbreviations.

$d$  = specific gravity.

$d_{20^{\circ}}$  = specific gravity at  $20^{\circ}$ , compared with water at  $15^{\circ}$ .

$d \frac{20^{\circ}}{4}$  = specific gravity at  $20^{\circ}$ , compared with water at  $4^{\circ}$ .

$\alpha_{D20^{\circ}}$  = optical rotation at  $20^{\circ}$ , in a 100 mm. tube.

$[\alpha]_D$  = specific rotation.

$n_{D20^{\circ}}$  = index of refraction at  $20^{\circ}$ .

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

$n$  = normal.

Acid no. = acid number; ester no. = ester number; sap. no. = saponification number.

g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Miltitz, near Leipzig, October 1, 1907<sup>1)</sup>.

Although in the past half-year business in our industrial branch of the essential oils has throughout been very brisk, and a considerable increase in the turnover can be recorded even as compared with the previous year, we believe that the cause of this will be found less in a continuation of the flourishing state of the trade, than in the extraordinary movements in the prices which some of our articles have experienced. As a matter of fact, for some considerable time the voices of those who count upon an imminent reaction in the commercial situation have predominated, and it cannot be denied that without doubt numerous arguments in support of the pessimistic outlook upon the future might be brought forward. Above all, the money market which remains in a state of tension in spite of a certain relaxation which has taken place during the last few weeks, justifies a feeling of anxiety, and it is impossible to give at once an affirmative answer to the question whether a brisk business is likely to develop during the autumn months. Meetings of monarchs, and the Peace Conference, fortunately are a guarantee that a disturbance of the continued peaceful development of our German commerce need not be feared, and that the unrest in Morocco will not lead to international complications of a serious character. In the Anglo-Russian agreement just concluded, we also see an important factor for the maintenance of the world's peace, as it serves above all to reduce to a large extent the tension between the two principal powers in the Far East which threatened to assume a somewhat serious aspect.

In Germany, the trade with all the branches which come under consideration for the consumption of our articles was brisk, and proved satisfactorily that for the present here at least no real grounds existed for the pessimistic outlook upon the future. In the commercial intercourse, the lack of definite official regulations dealing with the use of essential oils, essences, etc., in the trade of foodstuffs, is felt more and more, because (as has been proved by the numerous matters in dispute in recent times) the opinions of experts on such questions are occasionally absolutely contradictory. We hope, in the interest of the affected industries, that the German Government may soon find occasion to provide a lasting remedy.

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<sup>1)</sup> The commercial part of this Report has been compiled during September.

Our two branches, at Bodenbach and London, were extremely busy during the summer months, and the turnover at both of them shows a considerable increase as compared with the previous year. Although no definite basis has yet been found for the Austro-Hungarian "Ausgleich", and the result of the negotiations is still very uncertain, our experience does not enable us to support the view that this state of uncertainty has up to the present exerted any unfavourable influence whatever on the trade. In the United Kingdom, the past half-year also shows favourable figures, but business can on the whole only be characterised as slow and difficult. This must be attributed in the first place to the unsatisfactory position of the wholesale soap industry, to which we have already referred in our last Report, and which continues in face of the high prices of the raw material, but which, it is hoped, will soon give way again to normal conditions.

Trade with the British Colonies was not particularly lively, but in India, where the European perfume and soap manufacture is more and more appreciated, a brisk demand existed, especially for synthetic perfumes.

Our New York branch has also worked with increasing success. As far as the statistics have been made up, the value of our exports to the United States shows a really important increase over that of the corresponding months of last year. The prospects for the autumn trade are not unfavourable, and a satisfactory result appears certain again this year. How much the export of essential oils from the Leipzig district to North America has grown during the last few years, is clear from the statistics of the United States Consul at Leipzig, which show the following figures for the two last fiscal years (July 1 to June 30):

1905/6	\$ 197083.91
1906/7	„ 267454.54.

The recently published official figures of the essential oils imported and placed on the market in the United States in 1906 also show a considerable increase in the total import, which came to 2.79 million dollars, equal to an increase of 14 % over that of 1905<sup>1)</sup>. Our Leipzig industry of the essential oils has consequently every reason to be proud of its progress in the export to the United States.

Our readers may also be interested to know that the import of essential oils in the Philippines has increased from \$ 4358 in 1905 to \$ 5655, and that Germany's share in these figures amounted to no less than \$ 2426 in 1905, and \$ 4549 in 1906, whilst from the

<sup>1)</sup> Report of the Commercial Expert at the Imperial Consulate-General at New York. *Nachrichten für Handel und Industrie* 1907, Nr. 84.

United States the import is not worth mentioning. Although it is here only a question of small amounts, the above figures may give food for thought to the American colonial enthusiasts.

In order to meet a want which had been felt for many years, we have on the last of May of this year moved the whole of our New York business into more convenient and commodious premises (82 and 84, Beekman Street).

Under the beneficial influence of the growing mutual confidence, the relations with France have further improved in the most pleasant manner; and Italy, where unfortunately the appreciation of good qualities makes only very slow headway, also showed great interest in our articles.

In Switzerland, the new Patent Act, which is due above all to the diplomatic action of Germany, is expected to come soon in operation. Its most important innovation for the chemical industry is naturally this, that manufacturing processes can now also be protected by patents, which was impossible under the Act hitherto in force. The only inventions which cannot be patented in future would be: inventions of chemical substances and of processes for the production of chemical substances, in so far as they relate to the nourishment of human beings and animals, and inventions of remedies, foods or beverages for human beings and animals, other than those produced chemically, and also inventions of processes for the production of such articles. We can only give a joyful welcome to the new law, especially in the interests of the industry of synthetic perfumes, which under the existing conditions suffered particularly heavily.

Spain's political and commercial crises have unfortunately not yet come to an end, and that country is not able to recover completely from the economic misery which was brought upon it especially by Osman's portentous Alcohol Act some three years ago. This Act, hated for good reasons, has now at last, after obstinate protests on the part of all affected industries, been amended so as to afford some relief. Unluckily, the reforms are not sufficiently comprehensive to make an early revival of the badly ruined trade appear probable, the more so, as the negotiations for commercial treaties with other countries, which have now been pending for nearly a year, have not yet come to a definite conclusion. The Moroccan trouble forces new and enormous burdens upon Spain, for which it will hardly be able to find any equivalent whatever. The internal political dissatisfaction is growing daily, but unfortunately neither the people nor the Government appear to be sufficiently energetic to put a check to the state of uncertainty, and to render a return to a healthy prosperity possible.

The economic improvement of Russia has made further good progress during the last few months, and particularly the prospect of a

favourable, and in some districts even excellent harvest with high prices of grain ruling on the world's markets, assists in further raising the confidence in this powerfully absorptive country. Satisfactory prospects of the harvest not only increase the purchasing power of the country in the interior, but also pacify the minds of the country population, and enable one to forget the dark stains left in so many places in the course of last year by robbery, murder, and pillage.

The relations with the Balkan States were regular, and although occasionally, and especially in Turkey, difficulties arose in the payment of accounts, these countries are also gradually becoming more important.

With regard to the other European countries, nothing of importance is to be said.

The state of affairs in Morocco, disturbed by the Franco-Spanish intervention, calls for no special comment, as our products are only consumed on a very modest scale in that country. But we regret to have to put on record that the financial crisis prevailing in Egypt has not been without injurious effect on the sales to that country. In a report of the German Consulate of Cairo it is particularly recommended to exercise great caution in granting credit for new orders, but where the goods have already been supplied, not to insist too strongly, in the present difficult times, on the strict carrying out of the terms of payment. In the opinion of the International Chamber of Commerce in Cairo, there are absolutely no grounds for serious fears, as the financial crisis will probably retain a local character, and not permanently affect the prosperity of the country. Algeria continues to occupy a place among the most valued markets.

Among the Central American republics, Mexico now as heretofore demands the greatest amount of interest; the prosperity of that country continues to grow, and its purchasing power justifies the most sanguine hopes. A less pleasant picture afford the neighbouring States, which are all more or less ruined in consequence of the internal and external disorders, and which for the present cannot come under consideration for business of any importance.

In the Argentine, the overloading of the markets with imported goods has lately given rise to serious anxiety. Although a section of the Argentine commercial world had in recent times, through several heavy failures, been somewhat seriously affected, the imports have increased further under the effect of good harvest results, and this may possibly soon lead to further critical consequences if the pace of the importation does not slacken to some extent. In our own goods we can report a brisk business during the past half-year, but no unhealthy increase in the inclination to buy has been observed by us. It would therefore appear that the purchasers who come under consideration for our articles, have remained more or less unaffected by the crisis.

The state of affairs in Brazil is best illustrated by the report of the Commercial Expert at the German Consulate-General at Rio de Janeiro, according to which the value of the imports since the year 1901 has increased by 55,3 0/0, that of the exports 30 0/0. Whether and in how far the import duties which have lately been taken in contemplation, will also affect the importation of our goods, is for the present an open question.

With regard to the Far East, the sensational news which has recently reached us from America, of the imminent introduction of the gold standard in China, has no doubt excited a lively interest, but in view of the enormous difficulties connected with the conversion of a country without a standard into one with a gold standard, the report does not meet with much credence. For the present at least it would seem that a change in the Chinese financial situation is out of the question.

The favourable situation in Japan, to which we referred in our April Report, has unfortunately not lasted long, for the period of economic development after the Russo-Japanese war, which brought with it, as a secondary symptom, a time of wild speculation, has been followed already in the first months of this year by a severe reaction in the form of an enormous fall in the Stock Exchange quotations. Characteristic of Japanese enterprise is the fact, mentioned by the *Osaka Asahi* that between July 1905 and the end of 1906 no fewer than 3336 new companies with a capital of 605 1/2 million yen have been formed, whilst 580 existing companies increased their capital by 246 million yen. With the mania for speculation which permeates the whole people, shares came into the hands of small folk, exactly as at the time of the bubble-companies in Germany in the seventies, and senseless inflation led to an unhealthy state of affairs which could only end in a collapse. A large proportion of the newly floated companies has again disappeared from the face of the earth, but it will be some months before the confidence in the banks which have been engaged in these enterprises, and in the various affected branches of industry themselves, is restored. In consequence of this, the desire to buy of Japanese consumers has fallen off to a not inconsiderable extent, and it was now and then difficult to induce the purchasers to carry out their engagements to take up the goods contracted for.

In the early part of June great alarm was caused by a Government decree, requiring that all drugs and pharmaceutical preparations which had been examined according to the Pharm. Japon. II. and had been provided with the corresponding seal, should pass into consumption before the December 31, 1907. This step caused a downright panic in the drug market, as, owing to the extreme slackness of trade, large stocks had accumulated in the hands of all

importers. Fortunately wiser counsels have prevailed, for, according to a publication in the Japanese Gazette, pharmaceutical preparations according to the requirements of the old Japanese Pharmacopœia II will still be admitted in the country up to the 31<sup>st</sup> December 1908. The final period for allowing the examination of pharmaceutical preparations by the Government laboratories according to the Pharmacopœia II has accordingly been extended to the 30<sup>th</sup> June 1908.

Contrary to previous information, we now hear that an official translation of the new Japanese Pharmacopœia on the part of the Japanese Home Office, is not contemplated. A German translation has been made by Mr. M. Hirayama, Director of the Hygienic Laboratory at Osaka, but has unfortunately not yet come to hand, so that we are compelled to postpone a discussion of the new Pharmacopœia. The Japanese Pharmaceutical Society has also ordered an English translation which, however, is not yet completed.

The important increase in the import of essential oils in Japan during the last three years, and especially Germany's share in it, is clearly seen from the following figures abstracted from the Customs statistics: —

	1906	1905	1904
Germany . . . . .	202 000 yen	123 000 yen	67 500 yen
The United Kingdom	77 000 „	61 000 „	31 000 „
France . . . . .	17 500 „	17 200 „	5 000 „
Italy . . . . .	9 000 „	8 600 „	—
Switzerland . . . . .	5 500 „	2 500 „	1 000 „
	311 700 yen	212 300 yen	105 100 yen

In examining the movements in the values of our articles during the last few months, we find fairly large fluctuations in both directions, owing to which, as already mentioned, the trade experienced a not inconsiderable revival. The abnormal weather has naturally greatly retarded the growth of a large number of oil plants, and has had a very injurious effect on their yield of oil, the first-named fact especially in the present instance having rendered the compilation of our Report in many cases particularly difficult.

We are pleased to say that our works — which have now for six years served their purpose, — have again reached the limits of their capacity, so that for the coming year we are contemplating large extensions to our distilling installation. In addition to the erection of a new extensive distilling hall, we have provided for an addition of 12 boilers to our boiler house, which will double our output capacity. Our power station has already been doubled this summer by the erection of a second steam engine of 400 H. P.

We are specially indebted to Dr. H. Hildebrandt, Privatdocent at the University of Halle o/S., for kindly allowing us to reproduce *verbatim*, under Pharmacologico-physiological Notes, the part which will interest our readers chiefly, of his work entitled "Neuere Arzneimittel. Auf Grund von Studien über Beziehungen zwischen chemischer Konstitution und pharmakologischer Wirkung unter Berücksichtigung der synthetisch dargestellten Arzneimittel" (Modern pharmaceutical remedies. On the strength of studies on the relations between the chemical constitution and the pharmacological action, with due regard to the synthetically produced pharmaceutical remedies), — a work which will be published shortly by the Akademische Verlagsanstalt, Leipzig.

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## Commercial notes and scientific information on essential oils.

**Almond Oil, bitter.** This article naturally suffers much from the scarcity of the raw material, the apricot kernels (see under Almond oil, pressed from apricot kernels), and as a consequence we were not always able to cover the requirements. We avail ourselves of this opportunity to call again attention to the fact that this oil, adulterated in a very clever manner, is frequently offered at low prices, and that it must therefore be called an article of confidence in the true sense of the words. We consider it necessary to make this statement, as the prices of our genuine unadulterated oil will probably be raised again shortly.

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G. Velardi<sup>1)</sup> has attempted to determine in how far a previous increase in the temperature affects the formation of the poison in bitter almonds, and what changes amygdalin experiences by the action of increased temperature. When heated to 103°, the almonds were still capable of splitting off hydrocyanic acid. If the temperature was raised to 150°, hydrocyanic acid was only then still developed, if the bitter almonds were mixed with a paste of sweet almonds containing emulsin. Therefore, while emulsin becomes inefficient about 103°, amygdalin is not yet attacked at that temperature. When heated to above 150°, amygdalin yielded in the presence of emulsin a constantly decreasing quantity of hydrocyanic acid. At 166° the hydrocyanic acid reaction only occurred after 12 hours, and towards 170° all the amygdalin was apparently changed. Pure amygdalin, when

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<sup>1)</sup> Boll. chim. farm.; accord. to Journ. de la Parfumerie et Savonnerie Françaises 20 (1907), 66.

heated rapidly, melts with decomposition at  $208^{\circ}$ ; when heated slowly it remains unchanged up to  $170^{\circ}$ , and becomes brown (without it being possible to determine a melting point) at  $180^{\circ}$ . The mass heated to  $180^{\circ}$  had a resinous character, and contained 4.09% nitrogen, whereas amygdalin only contains 3%. The product, however, still yielded with emulsin hydrocyanic acid.

A work by E. Bourquelot and H. Hérissé<sup>1)</sup> deals with the conditions of isomerism of the five known hydrocyanic acid glucosides: amygdalin, Dakin's isoamygdalin, Fischer's amygdonitrile glucoside, sambunigrin, and prulaurasin, which under the action of emulsin are all decomposed into d-glucose, hydrocyanic acid, and benzaldehyde, that is to say, yield oil of bitter almonds. We would only refer here to the original treatise.

R. J. Caldwell and S. L. Courtauld<sup>2)</sup> have investigated the hydrolysis of amygdalin by acids, with special regard to the behaviour of amygdalin towards enzymes, so that their work also throws light upon the reaction taking place during the production of oil of bitter almonds. Ludwig had first established that the action of hot dilute hydrochloric acid gives results analogous to those of emulsin, but up to the present no information had been given on the rapidity of the hydrolysis effected by acid. The authors found that if normal hydrogen chloride is employed, the hydrolysis at a measurable rate only takes place at  $60^{\circ}$  and above, and for this reason they made their experiments at  $60$  to  $80^{\circ}$ . The results show that, although amygdalin is finally split up by acid into hydrocyanic acid, benzaldehyde, and 2 mol. glucose, the glucose is split off in two stages; by careful hydrolysis it is possible to obtain as an intermediate product the mandelonitrile glucoside which Fischer obtained from amygdalin by the action of yeast-extract. The saccharobiose radical in amygdalin has in the hydrolysis by acid, under the same conditions, at least six times the resistance of maltose.

The same authors<sup>3)</sup> interested themselves in the question whether Fischer's mandelonitrile glucoside obtained by them in the hydrolysis of amygdalin, must be regarded as a glucoside corresponding to amygdalin, or as a mixture of stereo-isomerides corresponding to isoamygdalin. It is well known that amygdalin is converted by alkalis into isoamygdalin. The authors obtained from mandelonitrile glucoside by the action of barium hydrate, the isomeric prulaurasin, which possesses a higher rotatory power than Fischer's glucoside derived

<sup>1)</sup> Journ. de Pharm. et Chim. **26** (1907), 5.

<sup>2)</sup> Journ. chem. Soc. **91** (1907), 666.

<sup>3)</sup> Journ. chem. Soc. **91** (1907), 671.

from l-mandelonitrile; a third isomeride of mandelonitrile glucoside, sambunigrin, possesses a still higher rotatory power than prulaurasin. Prulaurasin is completely analogous to isoamygdalin; it is a mixture of two stereo-isomeric d- and l-mandelonitrile- $\beta$ -glucosides; sambunigrin must be the  $\beta$ -glucoside of d-mandelic acid.

If an aqueous solution of l-mandelonitrile glucoside is treated with a very small quantity of ammonia or 1/500-normal baryta water at 25°, prulaurasin is formed. The prulaurasin obtained from Fischer's glucoside melted at 123 to 125°. The individual glucosides differ from each other by their readily obtainable acetyl derivatives.

Amygdalin and isoamygdalin yield hepta-acetyl derivatives (m. p. 167° and 148° respectively), l-mandelo-nitrile glucoside and prulaurasin yield tetra-acetyl compounds (m. p. 136° and 120 to 123° respectively).

When emulsin is allowed to act on amygdalin, there occurs after some time, like with other enzyme reactions, a state of equilibrium; the formation of hydrocyanic acid ceases, although the enzyme and also amygdalin are still present. The explanation of this must be looked for in the fact that the enzyme, at a definite concentration of its decomposition-products, is no longer able to exert any action, or that it is also capable of producing the reverse reaction. In the reaction emulsin-amygdalin it is not definitely known whether both possibilities come under consideration for bringing about this state of equilibrium. Anyhow it is certain that the emulsin is not destroyed, as the reaction continues if the benzaldehyde is removed by ether. During the distillation, however, the reaction cannot proceed further, as the emulsin is decomposed by the high temperature. But as amygdalin must still be present, Rosenthaler<sup>1)</sup> made the experiment of adding some sweet almonds after cooling, and distilling afresh. On the first distillation, which was only interrupted when the distillate gave no longer a hydrocyanic acid reaction, 0,215 and 0,237% respectively were found; the second distillate then still yielded 0,012 and 0,011% hydrocyanic acid respectively. If no sweet almonds were added, no further trace of hydrocyanic acid passed over.

**Almond Oil, pressed, from almonds.** The prospects of the harvest in Puglia can on the whole be characterised as favourable, so that, if nothing untoward occurs, a fall in the prices during the present season may probably be reckoned upon. In the months of May and June the quotations were driven up by speculators to 299 marks per 100 kilos (against 180 marks in October 1906), and as this movement was supported by brisk enquiries from abroad, a quieting down of the market was out of the question. The small

<sup>1)</sup> Südd. Apotheker Ztg. 1907, 496, accord. to Apotheker Ztg. 22 (1907), 680.

stocks which are available up to the appearance of the new crop are still kept high, but if this year's fruit is once placed on the market, a corresponding drop in the prices will in all probability take place, provided that speculative intervention does not once more upset all calculations. In any case a good medium harvest is anticipated the yield of which is estimated at about 170000 bales. Reports from Sicily are also favourable.

**Almond Oil, pressed, from apricot kernels.** As early as February the stock of Damascene apricot kernels of the last harvest was completely exhausted, and since then the gang of speculators have successfully attempted to keep up the prices of old kernels, or to drive them still higher. In view of the lack of normal kernels, even inferior qualities from the most varied districts outside the Damascene territory were absorbed at very high prices. If at Marseille, a port which ranks second in the trade in apricot kernels, Damascus kernels were quoted in July already at 115 francs, this price was considerably exceeded in Hamburg, inasmuch as occasionally for qualities of unreliable origin up to 106 marks per 100 kilos were paid.

The Mersina quality, which is greatly inferior to the Damascus kernel, also fetched high prices of 98 to 102 marks. In consequence of these movements in the markets, and of the reports of a very small Californian crop which came to hand as early as May (September shipments were offered at about 133 marks per 100 kilos), the price of new kernels also advanced, the more so as the Damascus harvest was said to be considerably smaller than that of last year. Reports say that the shortage is about 4000 to 4500 bales, as compared with a crop of 8000 to 9000 bales in the year 1906. The prices of this year's kernels moved at first between 96 and 98 marks for September-October delivery, but it is said that Hamburg has lately been offering at lower figures, the report being about 90 marks for shipment from Damascus, whilst kernels of other origin are said to be worth only 84 to 86 marks. The flat condition of the almond market, which of course affects that of the kernels to some extent, has probably induced Hamburg to start a movement in another direction, but this may at any moment turn round about. It is naturally difficult to say how the market will shape itself in the future, but in any case, our informant is of opinion that though at first the tendency may be weaker, a scarcity must make itself felt later on. In Damascus a large proportion of the crop has already been disposed of, so that in November, December and January not much can be expected, at least of qualities which come under consideration for oil. For this reason we do not think that for the present we can hold out to our friends any hopes of cheaper prices of almond oil from apricot kernels.

**Angelica Oil.** For a time there was a distinct scarcity in this oil, and especially during the last few weeks stocks have everywhere become greatly reduced. For this reason the new distillate is awaited with anxiety, although it can hardly come to hand before the end of this month. Our own as well as the Thuringian cultivation have suffered rather much from the effect of the abnormal weather, and a satisfactory result can hardly be reckoned upon. The prices of the pure distillate will regulate themselves correspondingly.

After a long time we have once again had an opportunity of distilling Japanese angelica oil. The oil, obtained in a yield of 0,1%, possessed an olive-green colour, and its odour could scarcely be distinguished from that of the oil obtained from German roots (*Archangelica officinalis* Hoffm.). It had the following properties:  $d_{15}^0$  0,9081;  $n_D^{20}$  — 1°40'; acid no. 10,6; ester no. 39,8; not completely soluble in 10 vol. 90 per cent. alcohol; soluble in every proportion in 95 per cent. alcohol; when cooled in a freezing mixture, abundant quantities of white crystals (oxypentadecylic acid?)<sup>1)</sup> separated off.

**Anise Oil.** The Russian anise harvest has been much delayed by the unfavourable weather conditions, and reports giving estimated figures of the crop have up to the present not yet been received. For this reason we must limit ourselves to the general remark that the result is judged favourably both in point of quantity and of quality. In spite of this, the prices at the first anise market at Krasnoje kept unexpectedly high, as only 53 truck-loads had been brought in, instead of 100 to 150 trucks in previous years. It is not astonishing that the small supply found ready buyers, and that the tendency at the close of the market had to be characterised as advancing. At the second market larger supplies are expected, but at the same time higher prices, as some of the principal buyers who up to the present have stood entirely aloof, will then have to arrange for covering their requirements.

**Oil of Asarum Blumei Duch.** According to Asahina<sup>2)</sup>, the Chinese drug *To-ko* is the dried entire herb (with roots and rhizome) of *Asarum Blumei* Duch.; it contains 1,4% essential oil of a yellowish colour, and a sassafras-like odour;  $d_{15}^0$  1,0788;  $[\alpha]_D^{20}$  + 5°3'; acid. no. and sapon. no. 0. Of the constituents, eugenol, safrol, and a terpene-like body were detected. The drug met with in commerce under the name *Sai-sin* or *Si-sin*, whose mother-plant is said to be *Asarum Sieboldi*, originates, according to Asahina, also from *A. Blumei* Duch. and is consequently identical with *To-ko*.

<sup>1)</sup> Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 574.

<sup>2)</sup> Journ. of the pharm. Soc. of Japan 1907, 362.

**Bay Oil.** Bay rum, which is universally popular as a cosmetic for the scalp, is, according to H. Berger<sup>1)</sup>, an excellent preparation for the treatment of the skin in general. Washing the head with bay rum morning and night, and also repeated daily ablutions of the body with bay rum water, or baths in hot water to which bay rum has been added, are said to have an extremely refreshing effect, and to give a feeling of comfort after bodily exertion such as on marches etc. This is particularly valuable, as Berger himself has found by personal experience during a sojourn in the tropics. Washing the hands with bay rum water, is also said to render good services in cracked skin above the nail-folds. According to Berger, bay rum is unequalled in *Seborrhoea sicca capitis*, and is said also to arrest the falling out of the hair, and even to promote the growth of the hair. In the tropics, bay rum has also been found an excellent prophylactic against various skin-eruptions peculiar to the tropics, and as a preventive against mosquitoes. But, according to Berger, these properties only belong to genuine bay rum, produced in St. Thomas. It is difficult to see, however, why a good bay rum manufactured here should have less valuable properties in this respect.

**Betle Oil.** When isolating chavibetol from an oil of betle leaves originating from Java, we made the interesting observation that the oil in question contained, in addition to chavibetol, another, solid phenol, which has up to the present neither been produced synthetically nor been found in the vegetable kingdom. Although the oil only contained 1,8 to 2% of this substance, and we only had 8 gr. of the pure body at our disposal, we were able to clear up its constitution. The oil from which the mixture of phenols was abstracted by shaking with dilute caustic soda, had in the course of years acquired a dark-brown colour, and possessed the following physical constants:  $d_{15^\circ}$  1,0325;  $\alpha_D$  —  $1^\circ 55'$ ,  $n_{D20^\circ}$  1,51362. For the pure chavibetol we found after repeated fractionation the following values:  $d_{15^\circ}$  1,0690;  $n_{D20^\circ}$  1,54134, b. p.  $107$  to  $109^\circ$  (4 mm. pressure). In a freezing mixture it congealed to a crystalline mass which melted again at  $8,5^\circ$ , a fact which had not been observed before.

For the purpose of obtaining the new phenol, the distillation residue of chavibetol boiling above  $113^\circ$  (4 mm. pressure) was further fractionated, when an oil distilling constantly at  $137$  to  $139^\circ$  was obtained which solidified on cooling.

The compound purified from petroleum ether alone, or preferably from benzene and petroleum ether, forms long, colourless, downy needles of the m. p.  $48$  to  $49^\circ$ , and the b. p.  $139^\circ$  (4 mm. pressure). Its alcoholic solution is coloured deep green by ferric chloride. A

<sup>1)</sup> Therap. Monatsh. 21 (1907), 221.

alkaline solution of the phenol acquires very rapidly a dark red colour. Its odour is comparatively faint, and distantly reminds of creosote. The phenol dissolves readily in water.

Some of the properties mentioned above allowed the conclusion to be drawn that this body is a derivative of pyrocatechol. The analysis shows that to this phenol belongs the gross formula  $C_9H_{10}O_2$ :

I.	0,1560 g. substance:	0,4101 g. $CO_2$ ,	0,0978 g. $H_2O$
II.	0,1737 g. „	0,4593 g. „	0,1121 g. „
III.	0,1665 g. „	0,4400 g. „	0,1046 g. „
		Found:	Calculated for $C_9H_{10}O_2$ :

	I.	II.	III.	
C	71,69%	72,19%	72,07%	72,00%
H	6,97%	7,17%	7,00%	6,67%

The methoxyl-determination according to Zeisel showed that the molecule contained no methoxyl-group. The benzoyl compound produced by Schotten-Baumann's method forms coarse, faintly reddish prisms of the m. p. 71 to 72°. According to the combustion it is a dibenzoyl compound.

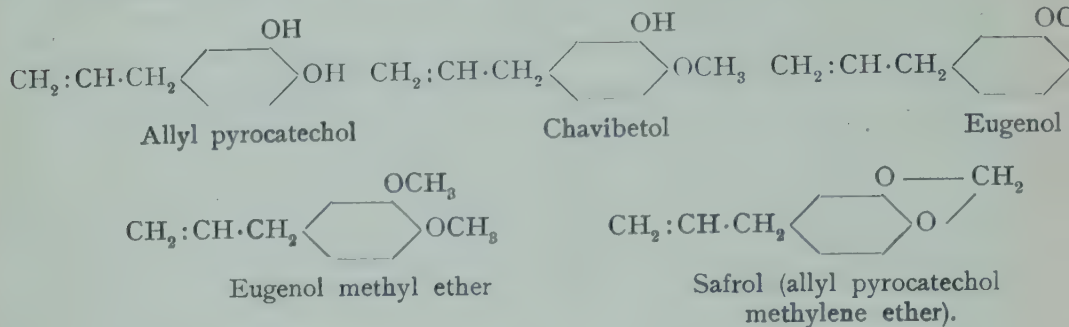
I.	0,1714 g. substance:	0,4836 g. $CO_2$ ,	0,0792 g. $H_2O$
II.	0,1680 g. „	0,4750 g. „	0,0804 g. „
		Found:	Calculated for $C_{23}H_{18}O_4$ :

	I.	II.	
C	76,95%	77,08%	77,10%
H	5,13%	5,31%	5,03%

The dibenzoyl compound no longer reacted with ferric chloride. A diacetyl compound was obtained as a colourless oil of the b. p. 157° (7 mm. pressure), 299° (atmospheric pressure). Although it showed an inclination to solidify, the quantity was so minute that it was impossible to isolate a solid substance. On methylating with dimethyl sulphate, the phenol was converted in eugenol methyl ether. The reaction-product driven over with steam had the following constants: b. p. 108 to 109° (4 mm. pressure), 248 to 249° (ordinary pressure),  $n_{D20} 1,53715$ . The fact that it was here indeed a question of eugenol methyl ether was proved both by oxidation with potassium permanganate, and by bromination. In the former case there resulted dimethylprotocatechuic or veratric acid of the m. p. 179 to 180°, in the latter, the characteristic tribromide of the m. p. 79 to 80° which solidifies when stirred with alcohol. A mixture of this compound with one produced from pure eugenol methyl ether, had the same melting point. Oxidation of the diacetyl compound with 2 per cent. permanganate solution unfortunately had not the desired effect.

The conversion of the divalent phenol to eugenol methyl ether supplied the proof that the body is allyl pyrocatechol, i. e. an

allyl-(1)-phen-(3, 4)diol, from which are derived both eugenol and chavibetol, and also safrol: —



Eugenol and chavicol could not be detected in the oil, although we made a thorough examination of the chavibetol fraction for this purpose.

We next turned our attention to the oil of betle leaves from which the phenols had been removed, and found in it still the following bodies. The lowest boiling portions of the oil (b. p. 155 to 162° 43 to 45° [4 mm. pressure],  $\alpha_D - 9^\circ 4'$ ) were tested for pinene, but no solid nitroso chloride could be separated off. The fraction distilling at 170 to 176° contained cineol. The iodol double compound purified from benzene, melted at 112°, and when heated with caustic soda liquor developed the characteristic cineol odour. An oil passing over between 100 and 107° (4 mm. pressure) boiled at ordinary pressure chiefly at 247 to 254°, and on oxidation with permanganate according to Tiemann's and Matsumoto's directions<sup>1)</sup> yielded a very small quantity of an acid melting at 179°, which quantity, however, was sufficient to identify it as veratric acid. From this it appears probably that the eugenol methyl ether was a constituent of the oil in question. Finally, caryophyllene, which formed the principal constituent of the phenol-free oil, could be identified by the nitrosate of the m. p. 158°. It was detected in a fraction with the following properties: b. p. 258 to 261°,  $d_{15^\circ} 0.9131$ ,  $\alpha_D + 6^\circ 34'$ ,  $n_{D20^\circ} 1.5072$ . A fraction of the approximate b. p. 275° and the further properties of cadinene<sup>3)</sup>, which was present in the oil examined by Bertram and Gildemeister, was not observed.

The foregoing examination has consequently shown that oil of betle leaves contains in addition to the already known constituents allyl pyrocatechol, a terpene, cineol, eugenol methyl ether, and caryophyllene.

<sup>1)</sup> Berl. Berichte 9 (1876), 937.

<sup>2)</sup> The m. p. of caryophyllene nitrosate is given in literature erroneously as 148°. According to our repeated observations it lies at 158° (comp. Report April 1904, 76).

<sup>3)</sup> Journ. f. prakt. Chem. II. 39 (1889), 355.

**Oil of Boldo leaves.** Up to the present, little was known of the chemical composition of oil of boldo leaves (*Peumus Boldus* Mol.)<sup>1)</sup>. For this reason we quote here briefly the results obtained by us in examining a distillate of our own. The physical constants of the brown-yellow oil were:  $d_{15^\circ}$  0,9567;  $a_D + 0^\circ 28'$ ;  $n_{D20^\circ}$  1,47928; soluble in 8 to 9 vol. 70 per cent. alcohol; acid no. 2,4; ester no. 11,2. It distilled between  $40$  and  $105^\circ$  (30 mm. pressure). Its odour greatly resembled that of Baltimore wormseed oil. The examination confirmed our surmise that the oil contained the body of the formula  $C_{10}H_{16}O_2$  which we isolated some time ago from American wormseed oil<sup>2)</sup>. By repeated fractional distillation we obtained a yellow oil boiling at  $74$  to  $76^\circ$  (2 to 3 mm. pressure),  $d_{15^\circ}$  1,0013, which possessed all the properties of the body  $C_{10}H_{16}O_2$ , above all the property of decomposing in an explosive manner, with evolution of gas, when heat was applied. The low-boiling portions of the oil consisted chiefly of p-cymene; they also contained cineol, and a terpene boiling about  $170^\circ$  which, however, could not be identified owing to its small quantity. We tested without result for phellandrene, limonene, and sylvestrene. The cineol was identified in a fraction of the b. p.  $175$  to  $178^\circ$ , by the iodol double compound of the m. p.  $119$  to  $120^\circ$ . When heating the recrystallised compound with caustic soda liquor, the unmistakable odour of cineol became noticeable. The p-cymene was detected in an almost inactive fraction boiling after the distillation over sodium at  $175$  to  $176^\circ$ , by means of oxidation with permanganate into p-oxyisopropyl benzoic acid of the m. p.  $154$  to  $156^\circ$ . When boiled with concentrated hydrochloric acid, the latter yielded p-isopropenyl benzoic acid of the m. p.  $253$  to  $255^\circ$ . In a fraction of the b. p.  $60$  to  $72^\circ$  (3 mm. pressure) traces of a higher fatty aldehyde were discovered; besides, the oil contains traces of a phenol which in alcoholic solution with ferric chloride gives a dirty green coloration.

The above examination established that oil of boldo leaves contains chiefly cymene, cineol (together about 30%), and the characteristic constituent of oil of chenopodium of the formula  $C_{10}H_{16}O_2$  (40 to 45%). Up to the present we have found nothing in literature to indicate that the oil had already been employed empirically as a remedy against worms, like Baltimore wormseed oil.

**Cajeput Oil.** The parcels of this oil received by us direct from our source of supply in Buru, have given satisfaction in every respect; the quality bears the stamp of expert distillation upon it,

<sup>1)</sup> Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 368.

<sup>2)</sup> We are still engaged in the examination of this compound, and will return in detail in our next Report on its remarkable behaviour.

and the quantities shipped were sufficient to meet the demand. The shipments via Macassar in which our own imports are not included amounted during the first five months, i. e. the period for which up to the present information has come to hand, to: —

	1752	baskets in the year 1907,
against	1061	" " " " 1906,
and	1408	" " " " 1905.

America still stands at the top as a consuming country; as already mentioned, the consumption of this article in Europe has suffered considerably from the good and cheap eucalyptus oils.

**Camphor Oil.** The prices of crude Japanese oil reached their highest level about the middle of April, when on the average 85/- per cwt. was asked, whilst white Japanese oil could be had at 72/-. Since then the market has shown very weak features, in agreement with the tendency of the camphor prices, and the prices of crude oil have gradually declined to about 43/- per cwt. Natural opinions as to the cause of this enormous drop in the prices differ, but the various reports received by us agree on the whole in that the competition of the Chinese camphor products has in recent times made considerable headway, and has been the principal factor in bringing about the change. On p. 24 of the present Report we give more detailed information as to the Chinese production.

From a report on the present position of the chemical industry of Japan, from the pen of the German Consul at Kobe, we abstract the following information<sup>1)</sup> on the articles camphor and camphor oil which interest us specially.

The Japanese Bureau of Monopoly carefully avoids the publication of details of its management, so that the available statistical material does not afford a clear view of the production.

The production of camphor during the last three years amounted in Greater Japan to

40235	piculs camphor and	34346	piculs camphor oil in 1904,
41023	" " "	34175	" " " " 1905,
41859	" " "	34833	" " " " 1906.

It should be taken into consideration that the above figures for camphor really come considerably higher, owing to the production of camphor from camphor oil, but how much this increase amounts to cannot be determined. The export-figures of the Custom's statistics from which the total annual production can be approximately calculated, were: —

<sup>1)</sup> Berichte über Handel und Industrie 10 (1907), 605.

	Formosa:		Kobe:		Total:	
	Quantity piculs	Value yen	Quantity piculs	Value yen	Quantity piculs	Value yen
1904:	24034	2199320	31408	3168197	55442	5367517
1905:	22430	2052933	22847	2556233	45277	4609166
1906:	21774	2222729	26565	3632785	48339	5855514

Assuming that the home consumption amounts to 10%, the figures of the last two years show a production, available for export, of fully 50000 piculs. How much of this belongs to Japan itself cannot be determined, as in Kobe, Formosan oil is also worked up for camphor; but in any case the camphor production in Japan has fallen off considerably during the last few years, and may possibly not amount to more than 8000 to 10000 piculs. Before the Formosan monopoly was extended to Old Japan, the production increased to about 30000 to 40000 piculs owing to the destructive cutting down of the trees, but it naturally soon diminished. In working up the Formosan camphor oil which was formerly placed on the market at Hongkong but now goes to Kobe — annually about 25000 to 26000 piculs — about 50% camphor, 18% so-called red, and 15% white oil are said to be obtained. Last year the Government prohibited the export of the white oil, which is used largely for disinfecting purposes and as a substitute of turpentine oil; this would explain the falling off in the export figures of camphor oil: —

	1905		1906	
	Quantity piculs	Value yen	Quantity piculs	Value yen
Oil:	12610	216122	7692	132502

In the camphor-export of Kobe, a portion, about 6000 piculs, of Formosan crude camphor is included; an equally large quantity of crude camphor is sold annually by the Government to the refineries at Kobe, viz.,

to the refinery Suzuki . . . . .	2500 piculs
„ „ „ Lucas & Co. . . . .	1000 „
„ „ „ Shono Kaisha . . . . .	2000 „
„ „ „ Fujigawa (Osaka) . . . . .	500 „

The attempts of the Government factory to produce safrol have been so unsatisfactory that the production has been given up completely.

According to the statistics of the German Empire, Germany comes first among the countries importing camphor, with 1013400 kilos, value 4560000 marks in 1904; in 1905 the figures were 890200 kilos, value 5786000 marks. The figures given in the Japanese Custom's returns are incorrect owing to wrong declaration.

The details on the importation of celluloid, and the proposed erection of celluloid works in Japan, which are also given in the

article under review, might not possess the same amount of interest for our readers, and likewise the information regarding the prices fixed between the Government and the selling agency for the various kinds of camphor.

Elsewhere<sup>1)</sup> the yield of camphor and camphor oil in the five Japanese camphor offices is estimated (but without mentioning the source of the information), for the year 1906 at 776743 and 842782 kin respectively, against 600347 and 652562 kin respectively in 1905. In Formosa the production in the years 1903 to 1905 was as follows: camphor: 3720263, 3389723, 2809190 kin; camphor oil: 2690229, 2720272, and 2544261 kin. The total export (of camphor and oil?) from Japan and Formosa in the last two years was: in 1905 5207244 kin, value 5316910 yen; in 1906 5544257 kin, value 5367510 yen.

In view of the continued decline of the Japanese and Formosan camphor production<sup>2)</sup>, the Japanese Government appears to be making very serious efforts to improve the camphor cultivation, both in Japan and in Formosa. The Vice-Minister of Finance Mizumachi stated, according to a Japanese report<sup>3)</sup>, at a conference in Tokyo with various officials of the Camphor Office, that the large sum granted by the Japanese Parliament for the forestry bounty, would be used exclusively for camphor plantations, and further, that the Government intended increasing the supplies and shipments in proportion to the demand, and meeting the wishes of the trade. For this purpose the commissioners had been sent last year to Europe and America.

A leading article in *The Chemist and Druggist*<sup>4)</sup> gives further details on the extent of the proposed reafforestation. In the principal district of Japan there are available a total of 206300 cho (1 cho = 2,45 acres) private lands, on which it is hoped to plant 361470000 trees; and also 625310 cho Government land with a possible amount of 1176810000 trees. From this is calculated a yield of 10844100 kin camphor, and 4337640 kin camphor oil. Naturally, the whole of the 200000 cho cannot be planted over in one year (in the two years 1904/1905 8734000 trees were planted out), and this would be carried out in ten years; but already in the fifth year after planting, a yield of 1084410 kin camphor and 433764 kin oil for every year's growth are hoped for. If the Government should succeed in inducing the owners of these private lands to plant them over with camphor trees, it would be possible after fifteen years to produce the above-mentioned 10 million kin camphor.

<sup>1)</sup> *Chemist and Druggist* 70 (1907), 815.

<sup>2)</sup> *Comp. Report* April 1907, 18.

<sup>3)</sup> *Oriental Druggist* 1 (1907), No. 14 (June).

<sup>4)</sup> *Chemist and Druggist* 70 (1907), 834.

But as, according to the statements of the Minister of Finance the trees would only be felled after fifty years, it must be assumed that the leaves and branches would be utilised for the production of camphor.

The world's demand for camphor is given in this article as 8 million kin (= 10,6 million lbs.), of which 70% are employed in the celluloid manufacture, and 2% go to the gun-cotton works; 15% are used for disinfecting and deodorising purposes, and 13% for medicinal preparations. The returns of the Japanese monopoly in 1906 are given as 1174889 yen, against 731592 and 705395 yen in the two preceding years<sup>1</sup>).

With regard to the extent of the camphor production in Formosa, a report from the American consul J. H. Arnold<sup>2</sup>) at Tam-sui in Formosa, gives detailed information, from which we abstract the following.

The Japanese camphor office in Formosa has prohibited the felling of camphor trees less than 50 years old. The number of trees of that age is small, and falls short of the estimates made up to the present, according to which the number of old trees would, at the present rate of cutting, last for less than 50 years. Large numbers of old trees are only found in the mountainous Eastern part of the island, within the savage district, and a further difficulty is found (supposing the savages were subdued) in the marshy soil of these mountain chains, which would probably demand large sacrifices in time and money for the making of roads for bringing the timber down. A further obstacle is the unhealthy climate of some districts, by which, for example in the district Daito, one third of the labour sent over there was incapacitated. There are constant complaints about lack of labourers, particularly of course in the vicinity of savage districts, where the wages (40 cents per day) are twice as high as in the civilised districts. The prospective yield for the current year is estimated by the camphor office there at 5 million kin crude camphor, and about half that quantity camphor oil; it is hoped that this yield will also be reached during the next few years, or may possibly even be increased somewhat. It is said that Formosa now supplies about  $\frac{3}{4}$  of the world's requirements of camphor; the remaining fourth comes from Japan and China. The Government bestows special care on the cultivation of seed and the transplanting of trees, which it has carried out partly by its own officials, and partly by agricultural societies or private individuals. Since 1900, 3 million young plants have been transplanted on behalf of the camphor office. This year a further half million plants are to be planted out, and this number it is hoped to increase to  $\frac{3}{4}$  million for

<sup>1</sup>) Chemist and Druggist 70 (1907), 815.

<sup>2</sup>) Daily Consular and Trade Reports, No. 2899, 19 June 1907.

future years. The trees planted in the higher, mountainous regions may not be utilised for 40 to 50 years; the seedlings planted in the plains, in view of the fact that their leaves are available after about 10 years, are put in rows close together, so that the plantation has more the character of a garden than of a forest. Apart from an occasional clearing of the soil, no particular attention or irrigation is required. In spite of the many kinds of harmful grubs, only about 6% of the young trees come to grief.

A very remarkable statement in the report is that there are two different varieties of the camphor tree, one serving for the production of camphor, and the other for that of camphor oil. The difference between the two kinds of trees, it is said, can only be detected by experienced people. During the last ten years, about 8 million young trees have been planted out in Japan. In China nothing has as yet been done in this respect, although a keen interest is taken there in reafforestation.

As a supplement to the above report may be taken the communication by the Tokyo correspondent of the *Times*<sup>1)</sup>, that the Japanese have decided to subjugate the district along the East coast of Formosa which since time immemorial has been inhabited by savages. The area, inhabited by about 100000 savages, comprises about 75000 square miles of the richest territory. 8000 Chinese, commanded by Japanese officers, have since last autumn already occupied 1328 square miles, in spite of obstinate resistance on the part of the savages.

Stimulated by the remunerative prices of camphor, the production in South China has been forced to the utmost, as we find mentioned<sup>2)</sup> in the last annual reports from the British consul Playfair<sup>3)</sup> and the American consul Gracey<sup>4)</sup>, both in Foochow.

The first-named states that the camphor export from Foochow, which in 1905 amounted to 4805 cwt., value £43039, in 1906 increased to 13585 cwt., value £185852. These figures point to an unprecedented destruction of trees, for which Gracey makes the Chinese, Japanese, and British responsible. In well-informed circles it is known that this fact must lead in 5 to 6 years to the ruin of the camphor industry in the province Fo-kien, as the trees there (and also in the adjoining province Chê-kiang) do not grow in close areas, but only here and there distributed in the Northern part of the province. No doubt the provincial authorities demand that, like in

<sup>1)</sup> Chemist and Druggist 70 (1907), 834.

<sup>2)</sup> Comp. the British Annual Report for 1905. Semi-annual Report April 1907, 19.

<sup>3)</sup> Diplomatic and Consular Reports, No. 3913, August 1907.

<sup>4)</sup> Daily Consular and Trade Reports, No. 2899, June 19, 1907.

Japan, for every tree felled five new trees should be planted, but this regulation, which promises results only after 40 to 50 years, cannot arrest the destruction of the older trees. Further, the American consul Arnold<sup>1)</sup> at Tam-sui states that this regulation only exists on paper, and that in practice nothing has as yet been done. Recently the Viceroy has imposed a tax of 1 tael (about 3 s. 2 d.) per picul camphor produced, and of 4 mace (about 1 s. 2 d.) per 100 lbs. camphor oil; the return thereof, about 8300 to 11450 dollars, is intended for purposes of reafforestation. The British report points to the remarkable fact that a large number of trees does not supply camphor, and recommends the foundation of a horticultural establishment to cultivate layers rich in camphor in a systematic manner. The consul proposes to send blossoms of the trees free from, and of such containing, camphor to Kew for examination. The prices of camphor kept mostly between 127 and 166 dollars per picul, but they fluctuated within very wide limits owing to the competition among the Chinese traders.

A Japanese report<sup>2)</sup> on the same subject estimates the camphor production in South China in 1906 at 4 million kin (= 2400 tons). Although this quantity appears to us to be taken rather high, there can be no doubt, after all that has been said above, which is also confirmed by a communication of the German *Handelsarchiv* (March 1907), that the export of camphor has increased considerably after the revocation of the monopoly granted to the Japanese for the province of Fo-kien. This article shares the fear of the above-mentioned consular report, that the trees will disappear in the course of time, at least in those districts which are accessible to the trade, and it quotes the following export figures: for 1904, 2219 piculs (2635 cwt.) and for 1905, 5363 piculs (6369 cwt.). These figures do not agree with the export figures (1421 and 4805 cwt.) for Foochow which the British consul had mentioned previously and now, and they may possibly refer to the export from the entire province Fo-kien.

Further reports have been received with regard to the countries which have recently commenced producing camphor, but whose yields up to the present are of no consequence in point of quantity.

It is well known that the cultivation of camphor in Ceylon at first encountered difficulties, as it was found impossible to obtain germinating seed. For this reason, other methods of cultivation were tried, which are referred to in detail in a work<sup>3)</sup> by the Government botanist Nock. They are: propagation by means of layerings,

<sup>1)</sup> Ibidem.

<sup>2)</sup> *Oriental Druggist* 1 (1907), No. 16.

<sup>3)</sup> *Chemist and Druggist* 71 (1907), 319.

by branch-cuttings, by root-cuttings, and by suckers. The only difficulty is said to be this, that but few plantations have mature trees to allow of cuttings being taken.

The Bombay Forest Department has made cultivation-trials with camphor trees in some districts of the Kanara range<sup>1)</sup>. To all appearances the plants thrive well there; the principal difficulty is how to procure the seed from Japan.

The Agricultural Expert of the Federated Malay States reports<sup>2)</sup> that an attempt has been made there to propagate camphor trees by layers. Owing to insufficient care, the first plantations with several thousand plants came to grief, but new layers have immediately been put out. This report does not recommend the cultivation of large areas, although the growth of the trees in the experimental garden is described as very satisfactory, which in comparison with the trees of the same age planted in Ceylon may be called very favourable, in spite of the fact that the Ceylon trees were grown at higher altitudes, which is considered more advantageous. Some 300 trees cultivated in the experimental garden at Batu Tiga, only a few feet above sea level, measured after two years already 12 to 14 feet.

The annual report<sup>3)</sup> of the American Bureau of Plant Industry expresses itself very favourably with regard to the cultivation-experiments made by the Bureau with camphor trees placed at its disposal by various planters in Michigan and Florida. The 30 lbs. camphor produced, yielded very satisfactory results on chemical and technological examination. It is believed that the camphor trees which occur only sporadically in Florida, can be multiplied with good results after careful investigation of the condition of the soil and irrigation.

In his report on the Kenia forests in the British East African Protectorate, D. E. Hutchins<sup>4)</sup> mentions a very valuable tree to which hitherto little attention had been paid, and which he calls "Ibean camphor tree". The external appearance of this tree is very remarkable; many specimens are of enormous size, 120 to 130 feet high and 8 to 11  $\frac{1}{4}$  feet in diameter. The green bark, green wood, and all herbaceous parts of the tree possess a strong camphor odour, and the structure of the tree as well as the build of the seed vessel point to a relationship with the camphor tree (*Cinnamomum camphora*). In a particular district 2,8 camphor trees were counted on an average per acre, and 51% of all the timber cut originated from these trees; in the highest instance,  $\frac{1}{3}$  of the total number of trees, and 78% of the felled

<sup>1)</sup> Chemist and Druggist 70 (1907), 540.

<sup>2)</sup> Board of Trade Journal of July 18, 1907; acc. to Journ. Soc. Chem. Industry 26 (1907), 889.

<sup>3)</sup> Oil, Paint and Drug Reporter 71 (1907), 25.

<sup>4)</sup> Chemist and Druggist 70 (1907), 974.

timber, belonged to this species. Unfortunately Hutchins does not say whether, as a matter of fact, camphor was isolated from this tree and detected. The Kenia forest covers an area of about 1 million acres, and the value of the trees is estimated at 23 million pounds.

The manufacturers of artificial camphor have, naturally, not been wanting in their endeavours to derive benefit from the advancing prices, and Japan looks with well-founded anxiety upon this competition, the importance of which, at times of normal camphor prices, has always been under-estimated. Recently artificial camphor has even been produced in Japan itself, namely by S. Otaui at Yonago<sup>1</sup>). Smell and colour of the powdery product resemble those of natural camphor, and the chemical examination made by Tabara is said to have given satisfactory results. Yet the correspondent does not believe that the synthetic camphor can be manufactured at a sufficiently low price to compete with the natural product.

The Meeting of the New York Section of the Society of Chemical Industry held on February 15<sup>th</sup>, was entirely devoted to camphor and its technology<sup>2</sup>). Papers were read by: H. H. Rusby, on the origin and production of camphor; G. Drobegg, on the purifying and refining of natural camphor; V. Coblentz, on the history of camphor and its use in pharmacy and medicine; R. C. Schüpphaus, on the technical application of camphor; F. J. Pond, on syntheses of camphor; J. E. Crane and C. M. Joyce, Notes on the analysis of camphor. Whereas the contents of the first five papers may be passed over here as well-known, the subject dealt with in the last paper may here not be devoid of interest. The authors first of all produced pure camphor by sublimation and subsequent threefold recrystallisation from proof spirit. The purity of the product was checked by the melting point: the sublimate melted at 177,5 to 178,5°, the product once recrystallised at 178 to 179°, and twice and thrice recrystallised camphor at 179,1 to 179,4°. The last-named product was employed for the determinations.

1. Sublimation. About 1 g. (weighed accurately) of the above camphor, is placed on a 2-in. watch glass, covered with another carefully ground 3-in. watch glass, and the whole heated for some time, say 30 minutes, on a metal dish over a very small flame. When all has been sublimed, the flame is removed, the camphor left to cool for 5 minutes, another ground, exactly fitting 3-in. watch glass is placed over the sublimed product, the latter dried for an hour in

<sup>1</sup>) *Chemist and Druggist* 70 (1907), 974.

<sup>2</sup>) *Journ. Soc. chem. Industry* 26 (1907), 380.

an desiccator, and weighed. Non-volatile impurities can be determined in the smaller watch-glass. The influence of the time during which the heating takes place is not of much importance, as is shown by the following data taken from the detailed tables of the authors: —

After heating for 10 minutes, found	97,05	0/0	camphor (mean of 4 tests)
" " " 20 " "	96,86	0/0	" " " 2 "
" " " 30 " "	97,04	0/0	" " " 3 "
" " " 45 " "	96,80	0/0	" " " 2 "
" " " 60 " "	96,68	0/0	" (one test).

The results therefore agree within  $\pm 0,5$  0/0; the correction required is  $+3,0$  0/0. This method is useful for rough but quick determinations.

2. Specific gravity. First of all tables<sup>1)</sup> were calculated, which give the specific gravities of solutions of the purest camphor in pure commercial benzene (of E. Merck), namely 0 to 30 g. camphor increasing by one half gram, dissolved in benzene up to 100 cc. Next, exactly 10 g. of the sample of camphor in question were dissolved in pure benzene in a 100 cc. graduated tube, and filled up to 100 cc. From the specific gravity, determined pyknometrically, like

the figures given in the tables, at  $\frac{20^\circ}{15,5^\circ}$ , the camphor content was calculated by means of the tables.

3. Polarisation. The optical method indicated by Landolt and modified by Förster, consists of the determination of the rotation of a solution of camphor in benzene, in Laurent's apparatus. The calculation is made according to the formula

$$c = 115,205 \left( 1 - \sqrt{1 + \frac{0,04367 \cdot \alpha}{l}} \right)$$

in which  $c$  represents the number of grams camphor of 100 cc. solution,  $\alpha$  the rotation,  $l$  the length of the tube in decimetres. The normal temperature,  $20^\circ$ , must be maintained exactly. The camphor was dissolved directly in an (American?) commercial benzene, as in the pyknometric determination, without previously separating the non-volatile substances according to Förster; but the figures obtained were 2 to 3 0/0 higher than those expected theoretically, because the benzene (as was found on examination) contained considerable quantities toluene and thiophene. With pure Merck's benzene the correct values were obtained, both with a Laurent's apparatus and with one of Schmidt and Haensch. The deviations fluctuated between  $+0,07$  and  $+0,14$  0/0.

The method of Arnost, basing on the volumetric expansion of petroleum ether solution, was found to be useless.

<sup>1)</sup> Reproduced ibidem p. 386.

Crude Japan camphor, examined according to these three methods, gave the following values:

1. Sublimation method: (mean of 4 tests, correction 2,77 %); content of camphor: 95,0 %, of non-volatile matter: 0,18 %.

2. Method of determination of specific gravity: 95,4 % (mean of 3 tests).

3. Polarisation method: 93,3 % (mean of 4 tests).

Judging from the m. p. 174 to 175,5°, the sublimate must have contained camphor oil, and for this reason the values obtained by method 1 must come generally too high. The still higher value of method 2 is explained by the fact that the specific gravity is influenced not only by the oil, but also by the heavier water from the moisture. This latter fact it was endeavoured to neutralise by recalculating the values of the table for moist benzene, whose specific gravity was determined at 0,8794 (dry 0,8782). Naturally, the quantity of water absorbed by the benzene depended upon the temperature. The determinations of specific gravity made with crude and pure camphor, with due regard to the moisture, gave for the former a content of 106,9 and 106,3 respectively, for the latter 101,4 and 100,2.

The high values observed with pure camphor clearly show the influence of the water on the density; for this reason the percentages of the crude camphor must be divided by 1,066. In spite of this, the mean of the values thus corrected, 94,5 %, remained too high, proving thus the presence of camphor oil.

An attempt to remove the impurities from the camphor according to Förster's<sup>1)</sup> directions, also remained without the desired result, as was proved by the figures obtained; even tests made with pure camphor led to losses of 2 to 3 %.

The polarimetric method is least of all influenced by the presence of impurities; the mean value obtained by this method is probably not far from the actual camphor-content. The difference between the results of the sublimation and polarisation methods should be taken into account as camphor oil, so that crude camphor would have the following composition: 93 % camphor, 2 % camphor oil, 5 % moisture, 0,18 % non-volatile substances.

The analysis of synthetic camphor encountered difficulties. The impurities of this product, intermediate products such as borneol, camphene, etc. sublime jointly with the camphor, are also soluble in benzene, and consequently increase the results of the methods 1 and 2. Method 3 fails, as synthetic camphor is inactive; this method can only be employed to differentiate between the natural and the synthetic product. A crude synthetic camphor gave the following results:

<sup>1)</sup> Berl. Berichte 23 (1890), 2981.

m. p. 150 to 155°; sublimate 98,2%; very impure. Various commercial products showed the following melting points: Portchester make, 171 to 173°, Schering, c. p., 171 to 175°, Schering, crude, 150 to 156°.

As stated by the authors, a correct method for the analysis of camphor, and especially of synthetic camphor, remains as yet to be discovered; the present methods can only suffice for approximate determinations.

**Caraway Oil.** As already mentioned by us in April, the area in Holland from which a crop was expected, was estimated this year at least as large as in the 1905/6 season.

According to official reports it was originally

12500 acres,	
against 11450 „	in 1906,
and 10610 „	in 1905,

that is to say, about 1000 acres more than in the previous year. This increased cultivation was chiefly in the provinces Groningen and North Holland. The severe winter, however, had elsewhere caused much damage, and as a result a great deal of land had to be dug up again, especially in Zeeland and Brabant.

In the beginning of the summer the condition of the plants was in Groningen good to very good, in Friesland fairly good, in North Holland good, in Zeeland fairly good, in Brabant middling to bad.

With regard to the area planted out with caraway in the principal districts, no official details have yet come to hand, but it is estimated as follows: —

Groningen . . . .	about 3750 acres
North Holland . . .	„ 5500 „
Zeeland . . . . .	„ 1250 „
Brabant . . . . .	„ 1000 „

Total about 11500 acres.

During the flowering season the weather was not favourable for the formation of the seed, but only the seed harvested in Groningen is designated as low. grade, whilst the quality in North Holland is judged “good to fine”, and in Zeeland and Brabant as “good”. On the whole, the seed is this year small-grained, and somewhat dark-coloured.

The crop is estimated

in Groningen . . . .	at 10 to 12 bales per acre
„ North Holland . . .	„ 8 „ 10 „ „ „
„ Zeeland . . . . .	„ 8 „ 10 „ „ „
„ Brabant . . . . .	„ 4 „ 6 „ „ „

From this a total result of about 110000 bales might be calculated, against about 90000 bales in the previous year. Although this shows

a surplus of about 20000 bales in favour of this year's harvest, it should not be forgotten that at the commencement of the new season no stocks worth mentioning of old seed were left on hand, in consequence of which a brisk demand gave rise to a firm tendency of the market. The farmers had therefore no difficulty in obtaining 17 to 17,75 florins for their caraway, according to quality. The tone is now as before very firm, and as in the meantime the prices, with a brisk demand, have advanced to 18,25 florins, it appears almost certain that in the further course of the season even considerably higher prices will have to be paid.

Of Norwegian caraway but little has up to the present been offered, and business fell mostly owing to the exaggerated notions of prices held by the producers. For the present it does not appear probable that from this quarter a pressure on the Dutch market can be expected.

**Cardamom Oil, Ceylon.** When examining Ceylon cardamom oil, Wallach<sup>1)</sup> found a hydrocarbon ( $d_{46} 0,846$ ) boiling at 165 to 167°, which with glacial acetic and hydrochloric acids yielded terpinene dihydrochloride (m. p. 52°). The surmise that it was a question of sabinene was confirmed by oxidation of the hydrocarbon with potassium permanganate to sabinenic acid (m. p. 56 to 57°). It was found that in the case of impure sabinene sabinene glycol was less suited for the identification of sabinene, than sabinenic acid, as impurities easily interfere with its crystallisation.

The correspondingly boiling fraction of oil of marjoram also yielded on oxidation sabinenic acid, and consists therefore of sabinene. The presence of terpinene (which had already been detected previously in the two oils) may, since the presence of sabinene in the two oils has been proved, be probably attributed to a conversion of this hydrocarbon into terpinene.

**Oil of Carrot Seed.** We have lately distilled an oil from the German fruits (not rasped) of *Daucus Carota* L., and found that its constants differed somewhat from those of the oil obtained in previous years. The brownish-yellow oil which possessed only to a slight extent the characteristic odour of carrots, was obtained in a yield of 1,26%, and had the following constants:  $d_{15} 0,9440$ ;  $n_D - 13^{\circ} 5'$ ; acid no. 2,2; ester no. 17,8; ester no. after acetylation 77,5; soluble in 1,8 and more vol. 80 per cent. alcohol.

♦ The constants of oils previously distilled by us were: —

Distillate of 1902:  $d_{15} 0,9226$ ;  $n_D - 23^{\circ} 16'$ ; acid no. 4,6; ester no. 30,6; soluble in 4,5 and more vol. 80 per cent. alcohol.

<sup>1)</sup> Nachr. K. Ges. Wiss. Göttingen 1907, Meeting of 20. July.

Distillate of 1904 from French carrot seed (yield 0,5 %);  $d_{15}^0$  0,9117;  $\alpha_D$  —  $18^0 18'$ ; acid no. 1,24; ester no. 51,93; ester no. after acetylation 95,7; not completely soluble in 10 vol. 80 per cent. alcohol; soluble in 0,4 and more vol. 90 per cent. alcohol; in this case rasped fruits had been distilled.

We are unfortunately not in a position to state whether the differences in the oils are due to differences in the uniformity of the material, or in the age (prolonged keeping?) of the fruit, or solely to the origin.

**Cassia Oil.** The quotation of 5/6 per lb. cif. mentioned by us in our last Report for 80 to 85 per cent. oil, has still been exceeded in the course of April. The prices reached their highest level with 6/- cif., and since then they have moved with slight set-backs down again to about 5/7. At such quotations the demand was naturally limited to cover only the most pressing requirements, and as the supplies have lately come in somewhat more freely, we think that a decline in the market is not improbable. But in the case of these Eastern products we are too much used to surprises, not to know that this opinion must only be regarded as the expression of personal sentiment. From the producing districts no fresh reports have come to hand.

**Champaca Oil**<sup>1)</sup>. In our Report of October 1906, p. 23 we mentioned that, after many fruitless attempts, we had succeeded in discovering again a certain source of supply for oil of champaca blossoms. The manufacturer of this oil, Mr. Anderson, chemist at Pasuruan, Java, when visiting us in September last year, gave us some interesting information on the origin of this rare oil. According to him, the oil is obtained from two different *Michelia* species, of which one produces white, and the other yellow blossoms. For the purpose of distillation white blossoms are chiefly used; they are sold by the piece, and give a yield of 0,0125% oil. According to C. L. Blume, Flora Javae, the white blossoms belong to *Michelia longifolia*, whilst *Michelia Champaca* bears yellow blossoms. As the two kinds of blossoms are not distilled separately, the oil supplied to us by Mr. Anderson is, as he himself informed us, a product which consists chiefly of oil from *Michelia longifolia*, and to a less extent of oil from *Michelia Champaca*.

As to the chemical composition of oil of champaca blossoms, nothing is yet known; for this reason we have commenced a detailed examination of the oil, the results of which are mentioned here.

<sup>1)</sup> Comp. Bericht April 1882, 7; Reports April 1894, 59; October 1894, 15; April 1897, 11.

With regard to the constants of the oil we would refer to the data given on page 23 of our Report of October 1906. We already called attention there to the fact that the oil has a feeble fluorescence, and consequently probably contains methyl ester of anthranilic acid, but the available quantity of the oil was insufficient for the exact demonstration of the presence of this compound.

When fractionating 300 g. oil at reduced pressure (8 mm.) the distillation commenced already below  $35^{\circ}$ , but the bulk distilled between  $68$  and  $83^{\circ}$ . This fraction consisted of linalool. By repeated fractionating, about 60% pure linalool were obtained from the oil, which showed the following properties: b. p.  $69$  to  $70^{\circ}$  at 3 mm. pressure,  $198$  to  $199^{\circ}$  at 749 mm. pressure;  $d_{15^{\circ}} 0,870$ ;  $n_D - 15^{\circ} 39'$ ;  $n_{D19^{\circ}} 1,47420$ . The phenyl urethane produced from it melted at  $65$  at  $66^{\circ}$ .

From the higher-boiling fractions ( $70$  to  $155^{\circ}$  at 5 mm. pressure), which had a particularly pleasant odour, ketones or aldehydes could not be isolated, but by treatment with phthalic acid anhydride a small quantity of geraniol could be abstracted, which was further identified both by oxidation into citral, and by conversion into the diphenyl urethane melting at  $80$  to  $81^{\circ}$ . The presence of eugenol methyl ether was shown to be probable, for a fraction boiling at  $248$  to  $255^{\circ}$  which had the odour of this compound, yielded on oxidation with potassium permanganate veratric acid melting at  $179$  to  $180^{\circ}$ .

Its silver salt was analysed.

0,2424 g. substance; 0,0902 g. Ag.

Found:	Calculated for $C_9H_9O_4Ag$ :
Ag 37,21%	37,37%

Of the known terpenes, none could be determined with sufficient certainty. The fraction (b. p. about  $180^{\circ}$ ) distilled over sodium, which came under consideration for terpenes, was very small. Its specific gravity was  $d_{15^{\circ}} 0,8516$ ;  $n_D - 7^{\circ} 40'$ . Bromination yielded no solid product.

The lowest-boiling portions of champaca oil, also unimportant in quantity, are characterised by a fruity odour, and consist of esters of methyl ethyl acetic acid. This acid could be obtained in the greatest quantity by saponification with alcoholic potash of the fraction of the oil boiling about  $130^{\circ}$ . The acid boils at  $176$  to  $177^{\circ}$  and is optically active,  $n_D - 16^{\circ} 40'$ . In the odour it reminds of tiglic acid. The silver salt recrystallised from hot water was analysed.

0,1637 g. subst.: 0,0845 g. Ag.

Found:	Calculated for $C_5H_9O_2Ag$ :
Ag 51,62%	51,63%

Methyl ethyl acetic acid appears to occur in champaca oil chiefly as ester of methyl or ethyl alcohol, but up to the present it has not yet been possible to detect these alcohols with certainty.

It is not improbable that the other higher-boiling alcohols of the oil (linalool and geraniol), are also present in champaca oil partly combined with methyl ethyl acetic acid. It could further be established that the acid also occurs in the oil in the free state, for on extracting 250 g. oil with 5 per cent. caustic potash liquor there was separated off, besides a small quantity of a still unknown phenol, methyl ethyl acetic acid.

Benzoic acid which had been detected in champaca oil on previous occasions, was not found in the oil in question.

The methyl ester of methyl ethyl acetic acid which has not yet been described in literature, could readily be produced by esterification of the synthetic acid with methyl alcohol and sulphuric acid. It boils at  $115^{\circ}$ , and has a pleasant fruity odour like the ester-fraction isolated from champaca oil.

**Oil of *Cinnamomum pedunculatum*.** In our last Report<sup>1)</sup> we referred to a work by S. Keimazu and S. Asahina on the oil from the bark of *Cinnamomum pedunculatum* Nees. We are now in a position to give some information on the same oil based on our own examinations.

The sample sent to us from Japan by a business friend, had a bright-yellow colour and the following constants:  $d_{15^{\circ}}$  0.9316;  $n_D^{20}$  —  $14^{\circ}32'$ ; not completely soluble in 10 vol. 70 per cent. alcohol; soluble in 1,2 and more vol. 80 per cent. alcohol. The oil contains about 6% phenols, which possess a cresol-like odour; the non-phenols contain phellandrene, and probably linalool.

**Cinnamon Oil, Ceylon.** In spite of the increase in our quotations, there was an extremely brisk demand for our distillate, which in point of quality is unexcelled, and in several cases we were unable to submit offers as our output could not keep pace with the orders. The prices of the raw material, cinnamon chips, remain firm without change, and lower offers were not considered. The shipments from Colombo in the period from January 1 to August 5 were 1463716 lbs. cinnamon chips, against 1333190 lbs. during the same period of 1906. It therefore appears that the export continues moving in an upward direction.

**Citronella Oil.** The prices of this important oil have now some months been moving slowly downwards, and at this moment have already arrived at 1/5 per lb. cif. Whereas early in April the

<sup>1)</sup> Report April 1907, 28.

tendency was still extremely firm, and no oil could be bought below 1/10, owing (it was said) to very short supplies which scarcely sufficed for carrying out previous contracts, the prices went down a few weeks afterwards to 1/9, and since then have fallen without intermission. The export-figures for January to September are as follows: —

1906	771416 lbs.
1907	855826 „

According to these, an excess of 84410 lbs. as compared with the previous year has now to be recorded<sup>1)</sup>. Under normal conditions such a surplus would hardly depress the market, but in the present year the situation is in so far abnormal, that the soap industry, particularly in the United Kingdom, has purchased less than last year, which has led to an accumulation of stocks in the European markets.

As a consequence the general tendency is weak, and in spite of the approach of the monsoon, which will interrupt the distilling season, we consider cheaper prices not at all impossible. It has lately become more difficult to form an opinion on the probable movement of the prices, owing to the fact that in the last few years the bulk of the trade in citronella oil in Ceylon has become concentrated in the hands of three important native traders, who work almost exclusively with the export firms at Galle. If these three traders should work together, it would of course, under favourable conditions, be possible to keep up the prices artificially.

Induced by the high prices which, as already reported by us, were due to the speculative action of one firm, a large number of planters in Java have again taken up the distillation, and the sources supplying Java citronella oil, which had given out long since, have recently again commenced to flow. As long as the consumers are able to absorb the supplies straight away, a fall in the prices is out of the question, but signs are not wanting that it is found a difficult matter to interest buyers in forward shipment at the present quotations.

It may engage the attention of our readers to learn that a factory has recently been established in Java, which is intended to work up the grassy residues resulting from the citronella oil distillation, into paper. Some ten years ago we already occupied ourselves thoroughly with the question of this utilisation, and we are pleased to know that it may now be reasonably expected to see the idea carried into practice.

**Clove oil.** The movement of the clove market during the summer months has again proved conclusively that reports on the results of the harvest, and as a matter of fact all information on this

<sup>1)</sup> The shipments from Jan. 1 to Oct. 28, 1907 amounted to 1039774 lbs., against 944153 lbs. in 1906, 1068974 lbs. in 1905, 990598 lbs. in 1904 during the same periods.

subject, must be accepted with the greatest possible reserve. Contrary to the view expressed in our April Report, that cloves would probably experience a considerable rise in the prices in the course of the summer, a change occurred already in the beginning of May, and since then the quotations have steadily declined. Against all expectation the harvest commenced this year very early, and the number of bales placed on the market in Zanzibar was in July already 6000 and in August 28000, (against 2000 in 1906 and 5600 in 1905). Under the influence of these figures, and of the fact that a few optimists estimated the result of the 1907/8 harvest at 150000 to 200000 bales, the quotations weakened further, until about the middle of September the fall was arrested. As the harvest has commenced early, a correspondingly early finish is anticipated. With regard to the probable further movement of the clove prices, we must refrain from expressing any opinion; we would only say that a group of interested persons also characterises the above estimates as much too high, and calculates the prospective result at only 50000 to 60000 bales.

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The *Diplomatic and Consular Reports*, Trade of Zanzibar for 1906, give under the heading "Cloves" the following interesting information:—

The total crop of cloves of the two islands was some 68000 frasilas,<sup>1)</sup> or 1,062 tons less than that of 1905, but there is every sign of an exceptionally large crop this coming season.

There was practically a small corner in this product during the year under review, owing to one firm being able to obtain possession of what is known as the duty cloves; cloves pay duty in kind at the rate of 25 per cent. of the crop. This, together with an early estimate that the crop would be an exceptionally small one, forced up the local prices considerably.

During the year a complaint was made in the home market that cloves were being sent home "in a damp or wet condition, or with more or less excessive moisture, the impression being that the cloves were by some means impregnated with water before shipment."

Merchants dealing with this product should thoroughly realise that if such practices exist as suggested by the Home Report it will have a very prejudicial effect on the home markets; buyers will be very chary in accepting produce with a prospect of a heavy rebate being made when re-selling.

It has been suggested, and the Custom-house authorities have been consulted on the matter, that when the shipments are being cleared through the Custom-house, some sort of examination should

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<sup>1)</sup> 1 frasila = 35 lbs.

be made and a certificate of condition be granted along with the Customs pass.

Merchants should remember that by a decree issued in 1903 the adulteration of produce is a criminal offence. Attention was also drawn to this fact in the *Zanzibar Gazette* of October 3, 1906.

**Oil of clove leaves.** From the Imperial Institute of the United Kingdom, the Colonies, and India, at London, we received an oil of clove leaves originating from the Seychelles, which resembles ordinary clove oil in the colour and odour. The properties of this oil are as follows:  $d_{15}^{\circ}$  1.0493;  $n_D^{20}$  —  $1^{\circ}40'$ ;  $n_D^{20}$  1.53329; about 87 % eugenol (determined with 3 per cent. caustic soda liquor in a cassia flask); soluble in 1 and more vol. 70 per cent. alcohol.

**Coriander Oil.** The coriander harvest in Russia, Moravia and Hungary has shown exceptionally favourable results both in quality and quantity, so that there is every prospect that in the coming half-year this important oil will again be available at the previous moderate prices. The quotations have continuously declined in the course of the summer, and it is therefore probable that a further reduction will take place in the next few months. We are this season working up considerable quantities of coriander, and hope that this will enable us to meet at all times the demand for our favourite own distillate.

**Elemi Oil.** A detailed work by Clover<sup>1)</sup> has appeared on the terpenes of Manila elemi oil. The author has collected on the spot a large number of samples of the resin which chiefly originates from *Canarium luzonicum* (according to Tschirch and Cremer from *C. commune*). In the native language the tree is called *pili*; the resin has the Spanish name *brea*. The manner of producing the resin resembles that of turpentine; the further working up for essential oil was carried out in the usual manner by steam distillation, during which, towards the end of the process, it was necessary to distil *in vacuo*, in order to drive the last portions of oil out of the resin which was then becoming more viscid. The commercial elemi is in the fresh state soft, sticky, and non-transparent; it has a pleasant odour, and a spicy, somewhat bitter taste. It dissolves readily in ether, chloroform, and benzene, — all but small quantities of water and a granular substance. In the other usual solvents, elemi only dissolves if large quantities of solvent are used; if a small quantity of alcohol is employed, 25 % of a white crystalline residue remain behind. For fresh elemi bought at Manila, the yield of oil often amounts to 25 to 30 %; Gildemeister and Hoffmann state a yield up to

<sup>1)</sup> Philippine Journ. of sc. 2 (1907), A. 1.

30%<sup>1)</sup> Clover collected 21 different samples elemi, and distilled them separately. The oils thus obtained showed considerable differences in the constants and composition, and were classified as follows: —

1. The oils 1 to 10 consisted of pure d-limonene.
2. Oils 11 to 19 contained a greater or smaller proportion of phellandrene; of these, oils 11 to 13 had a peculiar odour which could not be defined, and the boiling point observed at the commencement of the distillation was in these oils lower than in the remaining six oils of this group. According to this, there appears also to be present in the three oils a lower boiling terpene, probably pinene or an allied terpene. Of the remaining six oils containing phellandrene, one was lævorotatory, the other five more or less strongly dextrorotatory. Of the latter, the two oils with the highest dextrorotation had also a somewhat higher boiling point, whilst the three other oils appeared to consist of pure phellandrene. The lævorotatory oil contained chiefly l-limonene.

3. Oils 20 and 21, both rotating  $+4^\circ$  to the right, consisted of almost pure terpinene and terpinolene respectively.

The presence of terpinolene had hitherto not been observed in nature, and is therefore remarkable, the more so, as the oil containing terpinolene showed a very peculiar behaviour. The crude oil already boiled within one degree (Clover does not mention the boiling point), and had a rotation of  $+4^\circ$ . The reactions for terpinene and phellandrene had negative results; but a bromide of the m. p. 116 to 117° (with brown coloration and foaming) could be obtained in the form of brilliant scales (from alcohol). From this the presence of terpinolene might be assumed, whose boiling point Wallach determined at 185 to 190°, v. Baeyer (in a preparation regenerated from the tetrabromide) at 183 to 185°. The oil containing terpinolene was once more purified by treatment with potassium hydrate, distilled *in vacuo*, and had then the constants:  $d_{\frac{30}{15}}^{\frac{30}{15}}$  0,8360;  $\alpha_{D30^\circ} +1,7^\circ$ ;  $n_{D30^\circ} 1,4701$ ; b. p. 173,5 to 175° (at ordinary pressure); 80 to 81° (37 mm. pressure). Strange to say, the rotation had decreased considerably between the second and third distillation, although the oil had been prepared only on the previous day from elemi. In order to accelerate a possible change in the principal constituent of the oil, a portion of it was heated for 3 hours in a sealed tube on an oil bath to 200°. The distillate now showed a rotation of  $-7,5^\circ$ , and gave a not very powerful phellandrene-reaction (nitrite, lævorotatory, m. p. 119 to 120°). Five days later it was again intended to produce terpinolene tetrabromide from the purified oil, but instead of this there were obtained crystals of the m. p. 120°

<sup>1)</sup> Gildemeister and Hoffmann, *The Volatile Oils*, p. 491.

and having the appearance of dipentene tetrabromide, which melted after recrystallisation at  $125^{\circ}$ . In the meantime the rotation of the oil had also changed from  $+1,7^{\circ}$  to  $-1,6^{\circ}$ ; after a further five or six days, it had increased to  $-9,8^{\circ}$ , after another month to  $-34,5^{\circ}$ , a proof that a considerable alteration was proceeding spontaneously in the oil. After three more weeks the oil was distilled with steam; the distillate showed after drying  $\alpha_{D30^{\circ}} -38^{\circ}$ , and the conversion had consequently probably come to an end. The tetrabromide produced in various solvents melted after one recrystallisation at  $120$  to  $123^{\circ}$ , without becoming brown; after further purification at  $125^{\circ}$ . Phellandrene could no longer be detected by the nitrite-reaction, probably owing to the presence of a large quantity of dipentene. In Clover's opinion the almost pure terpinolene present in the original oil, (which had a particularly low boiling point), had consequently been converted by standing for several weeks, into dipentene, a small quantity of d-phellandrene, and an unknown lævorotatory terpene.

The high-boiling oil-portions from the individual species of resin had mostly a feeble lævorotation, and their specific gravities fluctuated between 0,9 and 1,03; they were chiefly mixtures of sesquiterpenes and oxygenated bodies. From an oil with the rotation  $\alpha_{D30^{\circ}} +71,6^{\circ}$ , a solid substance of the formula  $C_{15}H_{26}O$  could be isolated, which, however, during recrystallisation separated off in liquid form. In two species of resin, tests for the presence of amyrrin had negative results.

With the individual terpenes isolated from the oils, Clover has made a series of experiments, for details of which we must refer to the original work. With d-limonene he was able to state that heating to  $180$  to  $220^{\circ}$  has but a slight influence on the rotation, and that after heating to  $250$  to  $270^{\circ}$ , the isomerisation into dipentene proceeds very slowly. If the temperature is carried higher, to  $380^{\circ}$ , the formation of dipentene subsides before the polymerisation of limonene.

In the case of phellandrene, Clover observed that always the  $\alpha$ -modification of this terpene occurs in elemi oil. The rotation of the phellandrene diminished slowly already if left standing at ordinary temperature. With dry hydrochloric acid gas there was obtained an addition product which could not be distilled *in vacuo* without decomposition. A crystalline dibromide was not obtained even from the purest phellandrene which absorbed only 2 atoms bromine. When the phellandrene was left standing, crystals separated off on the glass walls of the bottle, the formation of which must be attributed to autoxidation of the phellandrene; after purification from hot acetic ester they melted at  $164,5$  to  $165,5^{\circ}$ , and had a composition corresponding to the formula  $C_{10}H_{18}O_2$ .

The terpinene of elemi oil yielded, on oxidation with 4 per cent. permanganate solution, considerable quantities of a crystallised acid which apparently represented a mixture.

With regard to the influence of prolonged storage on elemi resin Clover states that the limonene of the resin remains unchanged, but that the terpinene and phellandrene undergo far-reaching changes. The dry distillation of the resin yielded, in addition to 5 to 10% water, about 70% malodorous resin oils which passed over between 170 and 350°.

Oil of *Canarium Cumingii* Engl. Under the name "Pagsanguin oil" we received from the Bureau of Science of Manila an oil obtained from the resin of *Canarium Cumingii* Engl., which was mobile, pale green, almost colourless, and showed the following constants:  $d_{15}^{\circ}$  0,8627;  $\alpha_D + 11^{\circ} 3'$ ;  $n_D^{20} 1,47245$ ; soluble in 3 and more vol. 90 per cent. alcohol. On distillation the oil passed over from 158 to 183°; the bulk (70%) boiled between 165 and 177°. The principal constituent of the oil appears to be cymene.

## Essential Oils, Sicilian and Calabrian.

Our old friend, Mr. Eduardo Jacob at Messina, has again assisted us most kindly with his Report, which we reproduce *in extenso* hereunder: —

In my Spring Report I was already able to state that the export of the essential oils of this place, during the first three months of this year, showed a large increase as compared with the same period of the previous year. This increase has made further progress during the following five months, and even the exceptionally high prices of the last two months have not led to a falling off in the export to any marked degree, as is always the case during those months.

It is interesting to compare the figures of the current year with those of the three previous years. The export was: —

	1907 kilos	1906 kilos	1905 kilos	1904 kilos
in January . . . .	144 245	109 392	89 548	105 877
„ February . . . .	119 463	83 300	80 780	98 897
„ March . . . . .	127 679	85 294	80 157	91 132
„ April . . . . .	88 924	80 167	68 657	74 955
„ May . . . . .	65 725	96 571	53 032	57 932
„ June . . . . .	63 683	75 046	59 726	84 286
„ July . . . . .	70 911	39 396	48 219	52 584
„ August . . . . .	44 465	27 184	43 339	47 074
January/August	725 095	596 350	532 458	612 737

The export during these 8 months of the present year consequently exceeds not only that of the corresponding period of the two last years, but also of 1904.

Dealing with the individual essences, we had left **Bergamot oil** at a level of about 26 to 27 marks. These prices were at that time considered very high, and nobody would have dreamt that in the summer months prices advancing rapidly up to about 40 marks would have to be reckoned with. These extraordinary high prices, which had not been known for an age, must be attributed in the first place to a less favourable harvest, and secondly to a demand from abroad which was out of proportion to the limited stocks. Although at the moment only very small stocks of old oil are available, which probably do not exceed 5000 kilos and have to meet a three months' demand, the prices have declined somewhat during the last few weeks, owing to the fact that the owners had aimed too high, and had driven up their prices beyond all reason, so that the consumers preferred to retire from the contest and make-shift as long as possible with the stocks held abroad. To-day's price is about 37 marks cif. Trieste, but the most modest demand would probably suffice to rouse the owners again to action, and to induce them to ask higher prices.

The prospects of the new harvest unfortunately again cannot be called favourable. The cold of last winter has caused much injury to many of the trees planted in higher altitudes, so much so that they will scarcely yield any fruit at all this year. Along the coast, in the Southern extremity of Italy, the trees are rich in fruit, but to the North of Reggio, only a bare medium harvest can be looked for. Taking all in all, the opinion is that the new crop will turn out about one third smaller than that of last year; the general knowledge of this fact is reflected in the high prices asked by the manufacturers for new oil, and in the reserve of many manufacturers to sell even at those high prices.

The price asked for new oil moves at this moment about the level of 32 marks, but buyers abroad hesitate to conclude purchases at such high quotations. If the oil-content of this year's fruit should be found to be very high, the prices might possibly decline slightly; but if, as last year, the fruit should have a smaller oil-content, it is possible that the above-mentioned price will be maintained, and will become the ruling quotation.

**Lemon Oil.** In my Spring Report I gave expression to the view that this oil, which at that time stood at 12.50 marks, would go still higher if purchases continued to be made from abroad, and if foreign buyers could not at least for some time manage to do with the quantities of new oil already delivered up to that time. This, unfortunately, has not been the case; on the contrary, since that time many orders from local export firms have been placed to cover earlier forward sales at cheap prices, and moreover new important orders have been sent from abroad direct, at prices which were gradually

advancing more and more. America especially has been an indefatigable purchaser; during the first eight months of this year 367 138 kilos were shipped to that country, against 259 638 kilos in the same period last year, that is to say, an increase of 107 500 kilos.

It goes without saying that under those circumstances the manufacturers and speculators protected their stocks to the utmost, and only parted with them at constantly advancing prices; and that the two Associations had an easy task, in view of such a state of affairs, to control the situation, and manipulate the market after their own sweet will. As a consequence, the prices have since the beginning of March advanced rapidly to 13.50 marks in April and 14.50 marks in June, and finally reached their highest level in July with 17.25 marks.

Since that time the article fluctuates between 16.50 and 16.75 marks, according to the stronger or weaker daily demand. In view of the fact that we have still a two and a half month's consumption period before us, until the new oil arrives, the available stocks must be called extremely small and we have to face the possibility that the market will be completely sold out, and that it will be impossible to execute the orders coming in with old oil. A weakening of the price of prompt oil below the one mentioned above is in all probability out of the question.

Now if we consider that the last lemon crop has been very rich, and that the previous crop also was hardly less important, we may take it that the great increase in the consumption during last year cannot be attributed to temporary causes. On the contrary, the conviction must force itself upon us, that the annually increasing lemon oil production is not equal to the consumption which increases from year to year at a still greater rate, — in a word, that the world's consumption is larger than the oil production here. Under those circumstances we must rejoice in the fact that the new lemon crop does not look bad. Although here and there larger districts promise only a feeble harvest, the deficiency below the total production of last year does probably not exceed on the average 10 to 15 0/0, and this difference may easily be equalised by a greater oil-content of the fruit.

From this it appears that in the present year the causes are absent which would render probable an advance in the price of lemon oil beyond the limits reached to-day, and it is to be hoped that in the coming year this article will be subject to smaller fluctuations than during the past season. This may be expected all the more, as the two Associations had really no grounds for driving the prices of lemon oil to a higher level. The original idea leading to the founding of the Associations was that of bringing the lemon cultivation, which for many years had been carried on almost at a loss, into a better con-

dition. At that time there existed a disparity between the production and the consumption, and the latter was unable to absorb the quantity of lemon oil manufactured annually. Starting from the idea of regulating the supplies to the market here, and holding back in warehouses a portion of the harvest, it was hoped that by these means the lemon cultivation could be set on its legs again. This plan would have failed if the demand from abroad had not increased continuously and to such an extent, that it completely absorbed in the course of the last three years not only the large quantities produced each year, but also the stocks of old oil existing both in this country and abroad. Since the quantities produced and consumed do not balance each other and on the contrary the consumption exceeds the production, the lemon cultivation has been placed on a different basis which really renders interference on the part of the Associations unnecessary. It may therefore be assumed that in the coming season the local export trade may be saved from the mad fluctuations and sudden leaps of last season, and that the Associations will only then interfere again, when the price of the oil in their opinion should decline to too low a basis.

Simultaneous with the price of prompt oil, that of lemons has also advanced here; and influenced by the latter, also the prices of new oil of the coming harvest. When prompt oil reached the level of 17 marks, the highest price paid here for forward oil was 14.75 marks. Whilst from that time the price of prompt oil has only declined by 0.50 to 0.75 marks, that of forward oil has fallen by about 1.50 marks, and to-day it stands at about 13.25 marks for December-March delivery.

Under the prevailing conditions it is very difficult, if not impossible, to form a clear opinion as to the manner in which the movement of the price of lemon oil will develop during the next gathering season.

In view of the high prices of oil on hand, which will no doubt continue in force until the arrival of the new oil; in view of the fact that the stocks of old oil will by that time be cleared completely, and finally that the consumers abroad appear to be as short as the manufacturers here, and have no stocks of any consequence at disposal, so that they will appear on this market with a strong demand as soon as the new manufacturing season commences, — in view of all this it appears probable that the article in the course of the coming year will hardly go back below the approximate average of 12.50 to 14.— marks, whilst it does not seem impossible that new lemon oil in the first few months of the manufacturing season will at first occupy a mean position between to-day's prices of old oil, and those of new oil.

The lack of suitable labour, which is becoming more pronounced, the more feverish the infection of the emigration to America is spreading, has increased the wages here nearly three- to fourfold. This fact,

combined with the higher prices of the lemons, makes the cost price of lemon oil two to three times higher than formerly when the industry was in a state of general depression. Whereas formerly the manufacturer could be more easily induced to reduce his prices, as at the low prices his loss could not be very great, he would now have to face heavy losses if the price of lemon oil should drop to any considerable extent.

Apart therefore from all other considerations, it would appear that the fact just mentioned provides a sufficient guarantee that the prices of lemon oil in the next producing season will not fall much below the present quotations.

**Mandarin Oil** is entirely cleared out, and fetched up to the last 40 to 42 marks, according to quality.

The reports on the future crop are rather favourable.

**Orange Oil, bitter.** The prices of this oil have fluctuated in the course of the summer between 19.50 and 20.— marks. The available stocks are exceedingly small.

The new crop promises better results than that of last year.

**Orange Oil, sweet.** In our Spring Report we gave expression to the fear that the prices of the article, which then stood at 18.— marks, would probably harden with a later demand. This fear has unfortunately come true, particularly because the new orange crop, in spite of an almost over-abundance of blossoms, promises a very inferior result. The prices have advanced in the course of the summer to nearly 25 marks, and although they have now, in spite of the almost complete exhaustion of the available stocks, gradually declined to 22.50 to 23 marks, this can probably only be due to the approaching appearance of the new oil which is expected in about a month's time.

The prices asked by the manufacturers for new oil keep this article for the present at 21.50 marks, and even at this high figure very few people are prepared to sell. It is impossible to form already an opinion as to whether these prices will be maintained, or the manufacturers will be forced to reduce their quotations; it all depends upon the fact whether or not the fruit has a large oil content. In the former case further reductions in the prices asked by the manufacturers are not impossible; in the latter, the article might advance again — assuming that higher prices do not restrict the consumption abroad.

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**Eucalyptus Oil.** Business in all kinds of oil has been normal, and there were only slight fluctuations in the market prices. Lately the oil of *Eucalyptus polybractea* is receiving more attention; this is now produced in Australia in large quantities, and is said to be particularly suitable for certain purposes. For good "Globulus" oil there was always a keen demand, and the cheap kinds containing phellandrene also found a ready sale.

**Eucalyptol determination.** The value of eucalyptus oils containing eucalyptol depends exclusively upon their content of eucalyptol (cineol)<sup>1)</sup>. For this reason various methods for its determination have been worked out, of which the hydrobromic acid method and the phosphoric acid method are the best known. The latter has even been adopted by the new U. S. Pharmacopœia for the purpose of testing eucalyptus and cajeput oils. For the sake of completeness we will describe the two methods here again.

1. Hydrobromic acid method. In a highly cooled solution (freezing mixture!) of 10 cc. eucalyptus oil in 40 cc. low-boiling petroleum ether, (b. p. about 40°), absolutely dry gaseous hydrobromic acid is introduced until a precipitate is no longer formed. The pure white hydrobromide of cineol ( $C_{10}H_{18}O \cdot HBr$ ) formed is rapidly collected with a suction pump, and washed with cold petroleum ether. Into the filtered-off liquid, hydrobromic acid is again introduced, any precipitate formed is collected separately, and then added to the bulk. For the purpose of removing the petroleum ether, the cineol hydrobromide is left standing for a quarter of an hour in a vacuum; it is then rinsed with a little alcohol into a cassia flask, and decomposed with water. The cineol separated off is brought into the neck of the flask by the addition of more water, and the quantity of the oil read off the scale. By multiplying with 10, the cineol-content of the oil employed is obtained in per cent. by volume.

2. Phosphoric acid method (directions of the new U. S. Pharmacopœia)<sup>2)</sup>. 10 cc. oil are dissolved in 50 cc. petroleum ether, and to the well-cooled solution (freezing mixture!) concentrated phosphoric acid is gradually added, with stirring, until the white compound ( $C_{10}H_{18}O \cdot H_3PO_4$ ) separating off acquires a yellowish or pinkish shade. The crystalline mass is then filtered off with a suction pump, washed with petroleum ether, pressed between tiles to remove the last liquid portions, and decomposed with water. The cineol separated off is estimated volumetrically, and the result recalculated in per cent. by volume.

<sup>1)</sup> In the following pages the names eucalyptol and cineol are used alternatively.

<sup>2)</sup> Report April 1906, 73.

Both methods have the drawback that the addition-products of eucalyptol with hydrobromic acid and with phosphoric acid decompose very readily, which renders a quantitative separation very difficult. In consequence of this, the results obtained by the one or the other of the two methods are mostly too low, and in any case not absolutely reliable, as will be seen from the annexed table. This applies above all to the phosphoric acid determination, with which the results are almost without exception incorrect. If the undiluted oil is employed, the product separated off is so viscid, that it becomes most difficult to remove by pressure the portions of the oil which have not entered into reaction, whilst at the same time losses of cineol, owing to decomposition of the compound, cannot possibly be prevented. The separation of the compound succeeds better, if the oil is previously diluted with petroleum ether, as already mentioned in the description of the method given above; but in this case also the cineol is not removed quantitatively, as, according to Mossler's<sup>1)</sup> observations, a portion of the cineol is again abstracted from the reaction product by the petroleum ether (or does not enter into reaction at all). This is also found in washing the product with petroleum ether, when we observed partly also direct losses of cineol. It is, moreover, necessary to exercise great care in adding the phosphoric acid, as a slight excess already renders the originally crystalline product sticky; there is consequently added the risk that owing to an insufficient addition of phosphoric acid, not the entire cineol is combined. A really correct result is here more a matter of chance. According to these experiences we consider the phosphoric acid method totally unreliable and useless, and must decidedly caution against its adoption.

With the aid of hydrobromic acid we obtained results which were partly correct, but without being able to obviate in some cases quite considerable losses. The development takes place best from a saturated solution of hydrobromic in glacial acetic acid, but if the introduction of hydrogen bromide is prolonged, it is, even when using an intermediate vessel containing sulphuric acid, impossible to avoid that small quantities of acetic acid also pass over, and then exert a decomposing action on the cineol hydrobromide. This may of course occasionally give rise to considerable errors. Attempts to effect the development of the hydrobromic acid in a different manner gave no better results, and were for that reason again abandoned. A further difficulty in the quantitative separation of cineol hydrobromide is this, that the compound is extremely hygroscopic, and the absorption of water also takes place with decomposition. As it is impossible to

<sup>1)</sup> Zeitschr. d. allg. österr. Apoth. Ver. 45 (1907), 299.

carry out the filtration in an absolutely dry atmosphere, there exists here a further source of errors, and consequently neither the hydrobromic acid method can lay any claim to reliability. For this reason it appears to us to say the least very risky, to make on the strength of these methods definite statements with regard to the cineol-content of eucalyptus oils.

Cineol-determinations according to the hydrobromic acid method, and the phosphoric acid method.

Composition of the mixture in per cent. by vol.	Results obtained	
	Hydrobromic acid method	Phosphoric acid method
20 <sup>0</sup> / <sub>0</sub> cineol, 80 <sup>0</sup> / <sub>0</sub> turpentine oil	20,1 <sup>0</sup> / <sub>0</sub> ; 19,5 <sup>0</sup> / <sub>0</sub>	—
40 <sup>0</sup> / <sub>0</sub> „ 60 <sup>0</sup> / <sub>0</sub> „	39,8 <sup>0</sup> / <sub>0</sub> ; 32,4 <sup>0</sup> / <sub>0</sub> ; 23,6 <sup>0</sup> / <sub>0</sub>	—
50 <sup>0</sup> / <sub>0</sub> „ 50 <sup>0</sup> / <sub>0</sub> „	45 <sup>0</sup> / <sub>0</sub> ; 41 <sup>0</sup> / <sub>0</sub> ; 28 <sup>0</sup> / <sub>0</sub>	42 <sup>0</sup> / <sub>0</sub>
60 <sup>0</sup> / <sub>0</sub> „ 40 <sup>0</sup> / <sub>0</sub> „	63 <sup>0</sup> / <sub>0</sub> ; 54,8 <sup>0</sup> / <sub>0</sub> ; 45 <sup>0</sup> / <sub>0</sub>	53 <sup>0</sup> / <sub>0</sub>
70 <sup>0</sup> / <sub>0</sub> „ 30 <sup>0</sup> / <sub>0</sub> „	—	70 <sup>0</sup> / <sub>0</sub>
80 <sup>0</sup> / <sub>0</sub> „ 20 <sup>0</sup> / <sub>0</sub> „	77,9 <sup>0</sup> / <sub>0</sub> ; 73,8 <sup>0</sup> / <sub>0</sub>	—
100 <sup>0</sup> / <sub>0</sub> „ —	93 <sup>0</sup> / <sub>0</sub> ; 92,7 <sup>0</sup> / <sub>0</sub>	—

It is clear from the above table, and also from the one further down, that most eucalyptus oils contain more cineol than is determined by the hydrobromic acid or the phosphoric acid methods.

The absence of a really reliable method of determination of cineol has especially in recent times been felt more keenly, as nowadays in the purchase of oils great value is often attached to certain guarantees concerning their content of valuable constituents.

We have now found that resorcinol is a suitable substance for the quantitative separation of cineol from the oils. It is well known that cineol also forms an addition-product with resorcinol<sup>1)</sup>. The compound is already formed when cineol is shaken with an aqueous resorcinol solution, and it represents in the crystallised state needle-shaped crystals which melt at about 80°. They dissolve readily in alcohol, ether, and benzene, but with great difficulty in petroleum ether.

This compound is distinctly more stable than the two addition-products discussed above, but it also decomposes gradually on exposure to the air — more rapidly in a vacuum — giving off eucalyptol, so that finally only resorcinol is present. The same separation can also be observed when the compound is heated with water or petroleum ether.

Attempts made to carry out the cineol-determination thus, that the oil in question is shaken with resorcinol solution, the solid compound separated off is removed from the oil and then decomposed in a

<sup>1)</sup> Berl. Berichte 35 (1902), 1209.

cassia flask with the addition of caustic soda liquor, in order to determine in this manner the cineol volumetrically, gave no satisfactory results. On the other hand, the end in view was obtained by the observation that the cineol-resorcinol is soluble in a concentrated solution of resorcinol, and that its crystalline separation can be prevented, if from the first an excess of resorcinol solution is employed. In this manner it is possible to abstract the total cineol from the oil in question, and to retain it in solution in the form of the resorcinol addition-product, but for this purpose a highly-concentrated (50 %) resorcinol solution is required, whilst with less strongly concentrated solutions (even 40 to 45 %) no quantitative separation takes place. The quantity of the oil not consisting of cineol is ascertained by volume and thus the cineol-content determined.

The determination is carried out as follows: 10 cc. of the oil containing cineol are mixed in a cassia flask of 100 cc. capacity with so much 50 % resorcinol solution that the flask is filled for about  $\frac{4}{5}$ . The mixture is shaken thoroughly for 5 minutes, and the oil-portions which have not entered into reaction are brought into the neck of the flask by adding resorcinol solution, and their volume determined. By subtracting this volume from 10 the cineol-content of the oil is obtained, which is then expressed in per cent. by volume by multiplication with 10.

Oils very rich in cineol are suitably diluted beforehand with an equal volume of turpentine oil, as otherwise the cineol-resorcinol might crystallise out and cause the whole liquid to solidify, preventing so the determination. In this case the result must of course be multiplied with 2.

The volume of the oil remaining behind should not be read off too soon; the resorcinol solution should first of all be completely or almost completely cleared, and by occasionally turning and tapping the cassia flask, care should be taken that any oil-drops adhering to the walls of the vessel rise to the surface.

In order to test the reliability of the method we have prepared various mixtures and ascertained their cineol-content in the manner just described. We reproduce the results in the following table: —

1.	25 vol. % cineol	+ 75 vol. % turpentine oil;	found 27 %
2.	33 " "	+ 67 " "	" 34 "
3.	50 " "	+ 50 " "	" 50 "
4.	80 " "	+ 20 " "	" 80,5 "
5.	30 " "	+ 20 " "	+ 50 vol. % phellandrene; found 30 %
6.	50 " "	+ 20 " "	+ 30 " " " 50 "

We have also assayed a number of eucalyptus oils for their cineol-content, and in some cases also quoted the results obtained by the phosphoric acid method, which clearly shows the unreliability of the latter.

11.	$\Gamma$ $d_{15}^{\circ}$	$\alpha_D$	Solubility	Resorcinol method	Phosphoric acid method
1.	0,9185	+ 1° 13'	soluble in 2 to 3 vol. and more 70 per cent. alcohol	71 % by vol.	51 and 62 % by vol. resp.
2.	0,9186	+ 0°		82 % "	
3.	0,9142	+ 0° 40'		81 % "	40 " 51 % " "
4.	0,9241	+ 2° 25'		80 % "	
5.	0,9158	— 0° 45'		80,5 % "	
6.	0,9204	+ 0° 10'		85 % "	
7.	0,9221	+ 0° 26'		86 % "	
8.	0,914	+ 4° 55'	soluble in about 7 and more vol. 70 per cent. alcohol	77 % "	
9.	0,923	+ 8° 50'	makes a cloudy solution with 6 to 8 and more vol. 70 per cent. alcohol	70 % "	
10.	0,928	+ 0° 41'	soluble in 2 and more vol. 70 per cent. alcohol	94 % "	
11.	0,867	— 43° 40'	soluble in 0,5 and more vol. 90 per cent. alcohol with opalescence	29 % "	
12.	0,863	— 60° 25'		21 % "	

In the case of oil No. 5 the eucalyptol was again separated off from the resorcinol solution in order to test its purity, and the specific gravity, rotation, and refractive index determined. It was inactive, and had  $d_{15}^{\circ}$  0,9275 and  $n_{D20}^{\circ}$  1,46031. If it is considered that pure eucalyptol has a specific gravity of 0,928 to 0,930, the above result shows that apart from eucalyptol only such small quantities of other constituents of the oil pass over in solution, that they are of no consequence for the practical value of the method. The degree of purity of the eucalyptol separated off was also determined by fixing the solidifying point, which (as we have convinced ourselves) is also very useful for estimating the value of eucalyptol, as slight impurities already suffice to reduce the solidifying point considerably. Whilst according to our observations pure eucalyptol congeals at about + 1°<sup>1)</sup>, the above product separated from the resorcinol solution showed the solidifying point — 4,6°, a result which may be characterised as quite satisfactory if the unavoidable impurities dissolved mechanically are taken into consideration. It should still be mentioned that the solidifying point is determined in the usual manner<sup>2)</sup>. We cool the pure eucalyptol below the freezing point to about — 5°; in the case of less pure preparations it is sometimes necessary to cool even below that temperature. In this case also solidification must sometimes be started by inoculation with a little solid eucalyptol.

<sup>1)</sup> In one case we determined the melting point of pure eucalyptol at about + 1,5°; the previous statement that pure eucalyptol melts at — 1°, is therefore incorrect and should be amended.

<sup>2)</sup> Gildemeister and Hoffmann, *The Volatile Oils*, p. 176.

On the strength of the experience obtained by us with the resorcinol method, we can recommend it as useful. Over the two first-named methods it has the advantage not only of reliability, but also of a much more simple manipulation. It has also this advantage that the resorcinol can again be readily recovered and used afresh. It is only necessary to treat the solution (preferably previously freed from the oil which has not entered into reaction) with steam, when the resorcinol cineol is split up, and cineol distils over. The residue is then evaporated to dryness, and the resorcinol remaining behind is again ready for use.

As stated above, a concentrated solution of resorcinol dissolves, besides cineol, also other constituents of eucalyptus oil. We are at present occupied in investigating the influence exercised thereby on the exactness of the new method, and shall give further information in our next Report.

The determination of the bromine number which Mossler<sup>1)</sup> employs for judging the value of eucalyptus oil, is based upon the reaction of the less important, non-cineol-like constituents of the oil with bromine, so that the best quality oils, with the highest cineol-content, give the lowest bromine number. If the absence of possible admixtures of hydrocarbons which are apt to lower the bromine number, has been determined, it is possible, according to Mossler, in comparative examinations, to state that the oil is the richest in cineol which shows the lowest bromine number, as in the case of pure cineol the action of the bromine according to Mossler's method causes no addition or substitution; the bromine number allowed for cineol should not exceed 2.

We have checked Mossler's method on some oils whose cineol-content had been determined by the resorcinol method, and obtained the following results: —

Oil of	$d_{15}^0$	$n_D$	Cineol content %	Bromine number	Soluble in
I. <i>E. Globulus</i>	0,9186	$\pm 0^0$	82	51,6	2,2 vol. 70 per cent. alcohol
II. "	0,9185	$\pm 1^0 13'$	71	71,0	3,0 " 70 " "
III. "	0,9142	$\pm 0^0 40'$	82	56,7	2,5 " 70 " "
IV. <i>E. amygdalina</i>	0,867	$-43^0 40'$	29	161,5	0,5 and more vol. 90 per cent. alcohol, with opalescence
V. "	0,863	$-60^0 25'$	21	157,8	0,5 and more vol. 90 per cent. alcohol, with opalescence
VI. <i>E. rostrata</i> (?) (Algerian oil, free from phellandrene)	0,914	$\pm 4^0 55'$	77	58,5	about 7,0 vol. 70 per cent. alcohol

<sup>1)</sup> Comp. the present Reports, under Analytical notes.

This confirms on the whole Mossler's statement that oils rich in eucalyptol have a low, oils poor in eucalyptol a high bromine number. But the method has not been found useful in practice, as it is not safe to estimate the eucalyptol-content direct from the bromine number; for example, oil IV has, in spite of the higher cineol-content, a higher bromine number than oil V, whilst according to Mossler the reverse should be the case. Mossler further established that the action of the bromine on most essential oils shows constant values after six hours; only those oils which, besides adding, substitute much bromine show a pronounced increase of the bromine entering into reaction, when extending the time for reaction; but the values agree completely if the action is allowed to continue for equal times. We found that this view does not apply to eucalyptus oil, with which Mossler unfortunately made no experiments in this direction. After allowing the bromine to act for 20 hours we obtained the bromine numbers, for oil IV 189,4, for oil V 267,8, and for oil VI 77, numbers which do not speak for a uniform bromine-action. In view of the varying composition of eucalyptus oils, this behaviour is readily understood.

With regard to the general applicability of Mossler's method, we express our opinion in another place<sup>1)</sup>.

A sample of an oil from *Eucalyptus citriodora* Hook. of Indian origin, which we received from London, resembled exactly the Australian oils in its properties and composition. We determined the following constants for this oil:  $d_{15}^0$  0,8686;  $n_D^{20}$  1,020'; soluble in 5 and more vol. 70 per cent. alcohol; citronellal content 91,8% (determined by acetylation).

In a treatise on the eucalyptus species, G. Smith<sup>2)</sup> recommends that more attention should be paid to the cultivation of these trees, and that the results which we possess of the scientific examination of eucalypts and their oils should be utilised for the purpose of cultivating special species more for special objects.

Recent phyto-chemical researches have led to important results in this direction. Although a large number of chemical substances are present in the eucalyptus oils, there exists a certain regularity in their distribution among the individual species, and it is even possible from the venation of the leaf to draw conclusions as to the principal constituents of the oils<sup>3)</sup>. These groups are chiefly distinguished in this manner. The oil of the first group whose leaves have a thick midrib and marginal veins ending close to the edges of the leaf,

<sup>1)</sup> Comp. the present Report, under Analytical Notes.

<sup>2)</sup> Journ. Soc. chem. Industry 26 (1907), 851.

<sup>3)</sup> Comp. Report April 1902, 41; April 1906, 30.

contains chiefly pinene, but no eucalyptol or phellandrene. In the second group containing eucalyptol, the midrib of the leaf is less stout, and the marginal veins recede somewhat from the edge. The veins of the leaves of the third group whose oil contains phellandrene, are totally different: the midrib is very thin, and any feather-like venation is absent. In view of the different composition of the oils it is natural that they do not all possess the same medicinal value.

Although the value of the eucalyptus oil produced annually in Australia for medicinal purposes is £ 40000 to £ 50000, it is desirable to further develop the industry, and to take advantage of the enormous masses of raw material which are now wasted. As a large number of eucalypts are useless for economic purposes, those species should be eradicated and other more useful species should be planted instead. Two important points should also be observed, viz., firstly, that oils produced from young shoots of every kind (frequently in a good yield) have the same composition as oils from old trees; and secondly that the eucalypts are tenacious of life and after being cut down, soon shoot forth again afresh. If, therefore, a large area were planted with one particular species, and the young shoots were cut down by machinery, and distilled, the expenses of the oil manufacture would be merely nominal. Of the species which come chiefly under consideration, the following should be mentioned: —

*Eucalyptus Macarthuri*<sup>1)</sup>, for the geraniol manufacture. The oil contains at least 60 to 75%, in the form of geranyl acetate; in inverse ratio to the ester-content is the content of free geraniol in the oil. From young shoots 0,23% oil were obtained, the oil being 2% richer in ester than that of older trees. It should be possible to obtain this oil easily in any quantity, but it remains to be determined what is the most favourable time for collecting the material in order to obtain the best yield of oil.

l-Limonene and citral are found specially in the oil of *Eucalyptus Staigeriana*<sup>2)</sup>, known in Queensland as "Lemon scented ironbark", whose full-grown leaves yield 2,5% oil. This oil might be employed for many purposes instead of lemon oil(?) from which it differs particularly in the rotation. Smith mentions the following data for an oil of *E. Staigeriana*:  $d_{20} 0,87$ ;  $[\alpha]_D - 43,1^\circ$ ; citral 16%; geranyl acetate 8,3%; geraniol(?) 12,7%; not below 60% limonene; pinene and phellandrene were totally absent. The odour reminds of lemon oil, and does not resemble that of ordinary eucalyptus oil. The citral-content, which is higher than in lemon oil, is worthy of note, especially if the object in view is the production of a terpeneless oil.

<sup>1)</sup> Comp. Report April 1902, 38.

<sup>2)</sup> Comp. Report October 1906, 36.

*Eucalyptus citriodora* gives an oil very rich in citronellal (about 90%) in a yield of 0,58%.

The most numerous species are those which yield oils containing eucalyptol. For the production of such oils, *E. Globulus* and *E. Smithii* come chiefly under consideration; the former yields about 0,75% and the latter 1,5 to 2% oil, undoubtedly the best tree which is to be preferred for cultivation.

In an experiment with regard to the duration of the distillation, Smith found that 89% of the whole distillate passed over within the first 2 hours, 7% in the third hour, and 4% in the fourth. It may be accepted that in the first 2 hours the entire quantity of eucalyptol distils over, whilst the less volatile substances, sesquiterpenes, etc. remain behind.

Of volatile acids in the free state, only acetic acid was detected in eucalyptus oils. In the distillation water of *Eucalyptus amygdalina*, methyl, ethyl, isobutyl, and amyl alcohols were detected. The latter, esterified with eudesmic acid, is present in large quantity (about 57%) in the oil of *E. aggregata*<sup>1)</sup>. Other constituents of the eucalyptus oils worth mentioning are: eudesmol in *E. camphora*, aromadendral in *E. salubris*, piperitone in *E. piperita*, and sesquiterpenes in various species, especially in *E. haemastoma* up to above 50%.

As a continuation of J. H. Maiden's work: "A critical revision of the genus *Eucalyptus*"<sup>2)</sup>, the eighth<sup>3)</sup> part has now appeared, which forms a worthy addition to the previous parts, both in point of execution and get-up. In this number the following species are described in detail:

*Eucalyptus capitellata* Sm. [Synonyms: *E. congesta* R. Br., *E. capitellata* Sm., var. (?) *latifolia* Benth., *E. Baxteri* R. Br. and *E. santaliifolia* F. v. M. var. (?) *Baxteri* Benth.].

*Eucalyptus Muelleriana* Howitt.

*Eucalyptus macrorrhyncha* F. v. M. [Synonyms: Var. (?) *brachycorys* Benth., *E. scyphoidea* Naudin].

*Eucalyptus eugenoides* Sieb. [Synonyms: *E. scabra* Dum-Cours, *E. penicillata* Hort., *E. acervula* Sieb., *E. oblonga* D. C., *E. undulata* (?) Tausch., var. *nana* Deane and Maiden, *E. oleifolia* A. Cunn., *E. ligustrina* D. C. (*E. salicifolia* Cav.)].

*Eucalyptus marginata* Sm. [Synonyms: *E. pedicellata* R. Br., *E. floribunda* Hügel, *E. hypoleuca* Schauer, *E. Mahagani* F. v. M.].

*Eucalyptus buprestium* F. v. M.

*Eucalyptus sepulcralis* F. v. M.

<sup>1)</sup> Comp. Report April 1901, 33.

<sup>2)</sup> Comp. Report October 1903, 37; October 1904, 39; April 1905, 37; October 1905, 33 and April 1906, 35.

<sup>3)</sup> Sydney 1907.

**Fennel Oil.** The reports on the harvest in the Galician and Russian districts this year are on the whole again very favourable, although of course the abnormal weather conditions which have been observed throughout Europe, have there also not been without injurious effect. The result in Roumania is said to be very good, so that no doubt on the average the same fennel prices will rule as in 1906. The Macedonian article is kept very high, and for this reason can hardly come under consideration this season for working up into oil. For the rest, this quality is consumed almost exclusively in France; the 1906 crop (as we learn from a belated report) amounted to about 650 000 kilos, against about 800 000 kilos in 1905.

Lilla<sup>1)</sup> recommends that the fennel cultivation, for the production of oil, should be taken up in Italy, as it gives remunerative results. The average yield is 5 to 8 cwt. per acre, and the price per cwt. 45 to 60 francs. The time for sowing fennel (which according to Lilla, demands a not too moist, well manured and properly worked-up mould), commences at the end of January and lasts until the middle of February. The furrows are made 3 to 4 inches deep and 28 to 32 inches apart; 9 to 13 lbs. are sowed out per acre. When the young stalks are 3 to 4 inches high, the rows are thinned out, so that the plants are left 4 to 6 inches apart. The weeding and turning over of the soil should receive due attention. The harvest takes place in August.

**Geranium Oil.** The Algerian oil suffered again from great neglect, so much so that the producers were compelled to reduce their quotations from 30 to 26 francs, without meeting with any particular response on the part of the consumers. Although the first cut is said to have given a quantitative result below the average, and the second cut has also turned out very deficient owing to continued drought, we succeeded in purchasing some parcels at 24 francs, but this price is believed to be unremunerative, and in the last few weeks the tendency was less yielding. According to the official statistics, the export in the first 6 months of this year amounted to only 16700 kilos, against 29300 kilos in the same period of 1906. The mean value of the export only came to barely 25 francs per kilo, against 30 francs in the previous year. These figures speak for themselves.

The main reason for the unsatisfactory prices is of course to be found in the absolutely desperate condition of Réunion oil, which

<sup>1)</sup> Il Coltivatore; acc. to Bulletin de l'Office du Gouvern. gén. de l'Algérie 13 (1907), 211.

remains in a state of downright neglect, in spite of the Syndicate and of the reports of failures of the harvest which from time to time spring up again. All attempts to raise this article once more to a sensible level, have up to the present failed absolutely, and no improvement in this state of affairs can probably be expected in the near future, if the limited absorbing power of the consumers is not met by a proportionate restriction in the production. Although the shipments from Réunion in the first six months of this year were only 10372 litres, against 13792 litres last year, it remains to be feared, according to the reports received, that this deficiency will be at least recovered in the second half-year, and that consequently the position of this article is not likely to improve in the near future.

Palmarosa oil was equally neglected during the past months, and it is doubtful whether the high prices will remain in force for any length of time if the new harvest turns out at all favourable. Contrary to what used to be the case, the quotations for the new distillate have not yet reached us, and under the circumstances we must refrain from expressing any further opinion on this article.

Gingergrass oil continued to be scarce and dear, but the high prices have greatly influenced the demand. For this oil also, quotations for the new production are still absent.

**Hop Oil.** This article suffered from a falling-off in the demand, the cause of which it has not yet been possible to discover. The anxiety as to how hop-vines would come through the winter, was fortunately unfounded; the cool uncertain weather conditions no doubt prevented the rapid growth of the plants, but on the other hand protected them from insect pests and consequent diseases. If nothing untoward occurs, it may be expected — as far as the position in the various producing districts can as yet be surveyed, — that the hop harvest will be in every respect satisfactory, so that very moderate prices may be anticipated.

**Juniper Oil.** Since a few advantageous blank offers, which were probably only a manœuvre of the speculators, have been withdrawn, the Italian market shows a distinctly firm tendency, and it would appear to us that we may again expect this year high prices for good berries suitable for distillation. From Hungary and Bosnia no reports on the harvest have as yet come to hand. During the last few months there was a very brisk demand for all kinds of juniper oils, so that the prices had to be raised on several occasions.

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In recent times there have been many complaints, especially in England, about the want of uniformity of the oils met with in commerce. Umney and Bennett<sup>1)</sup> found the following differences: —

	English oil	Foreign oil
Specific gravity . . . . .	0,870 to 0,900	0,860 to 0,880
Optical rotation (100 mm.) .	— 10° to + 1°	— 3° to — 12°
Index of refraction . . . .	1,4820 to 1,4880	1,4770 to 1,4830

On fractional distillation there passed over:

	Of English oil:		Of foreign oil:	
	freshly distilled	old dist.	Hung. dist.	German dist.
below 160°	14 0/0	14 0/0	22 0/0	31 0/0
„ 170°	52 0/0	—	60 0/0	—
„ 180°	65 0/0	44 0/0	72 0/0	45 0/0
„ 200°	75 0/0	—	85 0/0	—
„ 210°	—	54 0/0	—	62 0/0
„ 265°	—	75 0/0	—	74 0/0

Similar results were also found by Bird<sup>2)</sup>.

Umney and Bennett propose the adoption of the following requirements for the British Pharmacopœia: “d<sub>15°</sub> 0,860 to 0,885; α<sub>D</sub> — 3 to — 12°; below 165° not more than 60 0/0 shall distil over. The index of refraction of the oil is of no importance, but it is advisable to determine the refractive index of the distillation-residue after 80 0/0 have been distilled off; this index should not be less than 1,49. Freshly distilled oil should dissolve in 10 vol. 90 per cent. alcohol. In older oil the solubility diminishes owing to oxidation, and the specific gravity increases at the same time.”

Parry<sup>3)</sup> also agrees on the whole with these statements. Bird attributes the differences occurring during fractional distillation to the fact, that the English oils are normal distillates, whilst the Hungarian oils consist of the more readily boiling portions. In our opinion this is explained by the fact that the Hungarian juniper oils are not distilled direct from the berries, but (comp. also Stroecker)<sup>4)</sup> are obtained as a by-product in the manufacture of juniper brandy, and consequently form the less soluble portions of the total oil. Stroecker estimates the annual production of juniper oil in Hungary at 30 000 kilos, but this figure certainly appears to have been taken too high.

<sup>1)</sup> Pharm. Journal **79** (1907), 131; Chemist and Druggist **71** (1907), 172.

<sup>2)</sup> Pharm. Journal **79** (1907), 130; Chemist and Druggist **71** (1907), 172.

<sup>3)</sup> Chemist and Druggist **71** (1907), 355.

<sup>4)</sup> Pharm. Post **38** (1905), 236. Accord. to Berichte d. deutsch. pharm. Ges.; Bericht über die pharmakogn. Lit. aller Länder für 1905, 67.

We would still refer here to a comprehensive work by J. Rodié<sup>1)</sup> on the properties and the composition of the oils of the various juniper species, which work, however, on the whole gives no new information.

**Oil of *Juniperus chinensis*.** According to examinations by H. Kondo<sup>2)</sup>, the essential oil of *Juniperus chinensis* appears to resemble very much, from a chemical point of view, the oil of *Juniperus virginiana*. The cedrol and cedrene isolated from the oil were chemically identical with those isolated from *J. virginiana*; but in their physical properties they differed rather considerably. For microscopical purposes, the cedrene from *J. chinensis* is, according to Sato, quite as suitable as the cedarwood oil which has been employed up to the present.

**Lavender Oil.** Since reports from all the producing districts have now come to hand, there can be no doubt that the result of this year's harvest must be designated as favourable, although late frosts in the spring have caused much injury to the plants in various districts. Copious rainfall in the months of May and June has not failed to exert its beneficial influence, so that this year an excellent blossom-material was available. On the whole, the commencement of the distilling season has been greatly delayed, as the abnormal weather conditions have also in the lavender districts naturally had a retarding effect on the development of the plants. In our Barrême distillery, work commenced at the end of July, and continued until the first days of September. In spite of ample precautions we were not able to increase our production this year very much over that of last season, as in the purchase of the blossoms the prices were driven up again as usual, and we were naturally unwilling to go beyond a reasonable limit. The price of our own distillate, which again this year shows no less than 52% ester, must be kept at a high figure, proportionate to the cost price, but in spite of this there is no lack of interest in our oil, and we have no doubt that the article will very soon be cleared out again.

The first essence market took place at Digne at the beginning of September, but without leading to any sales worth mentioning. In view of the good harvest, the purchasers had such poor notions of prices that the producers were not prepared to give up their stocks, and preferred to await developments. At the second market, at Sault, the transactions were also unimportant, but here an improvement was already noticeable in the demand, as it was not considered wise to let the opportunity pass without at least covering the most urgent requirements.

<sup>1)</sup> Rev. gén. Chim. **9** (1906), 444; accord. to Chem. Zentralbl. **1907**, I. 814.

<sup>2)</sup> Journ. of the Pharm. Soc. of Japan **1907**, 236.

As it was not possible to make any purchases worth mentioning, we are not yet in a position to reduce our selling prices in a manner corresponding to the actual harvest results, but we would point out that the longer the consumers are holding back their orders, the more yielding the manufacturers will become, and that consequently the movement of the prices will probably depend exclusively upon the demand during the next few months.

In our last Report<sup>1)</sup> we have already referred to the experiments in the cultivation of lavender made in the South of France. Lately<sup>2)</sup> this cultivation seems to receive all the interest it deserves, the more so as at the present oil prices the cultivation must unquestionably be very remunerative. The author of this article advises the landed proprietors not to wait any longer with cultivation experiments on a few acres, until perhaps others have pocketed the profits, but to make use of the opportunity offered by the present high prices.

The cultivation does not involve much trouble. When the soil is fertilised in the manner recommended by Zaccharewitz<sup>3)</sup>, the cost of laying out one acre of lavender is estimated at about 400 francs (say £ 16), taking 16600 young plants at 50 francs per 1000. In the second to the fifth years the net profit comes to about £ 15 per acre, in the sixth and following years to about £ 8 to £ 10.

**Lemongrass Oil.** As we anticipated, the backward movement of the prices has since April of this year made further progress, and the quotations have declined to 2<sup>1</sup>/<sub>2</sub>d. per oz. As large contracts had been made at 3d. per oz. (as already mentioned by us), there was very little inclination to buy when the market gave way further, and the consequence was a renewed fall. The following figures show in how striking a manner the production has increased in the season 1906/7: —

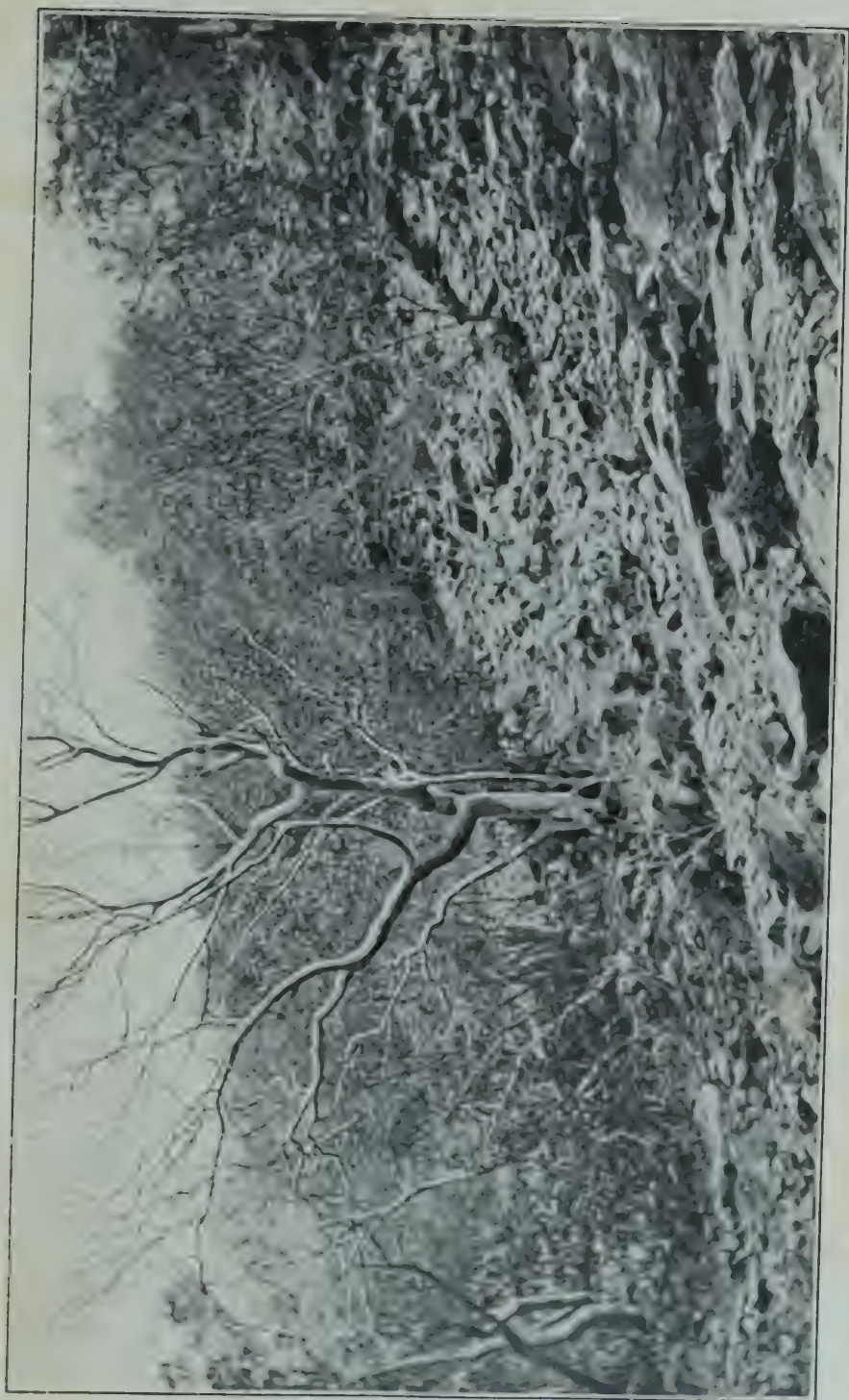
Between July 1, 1906 and June 30, 1907 there were shipped: —

to London . .	609 <sup>1</sup> / <sub>12</sub>	cases			
„ Havre . .	1267 <sup>5</sup> / <sub>6</sub>	„			
„ Marseilles .	1733 <sup>1</sup> / <sub>2</sub>	„			
„ Antwerp . .	129 <sup>2</sup> / <sub>3</sub>	„			
„ Hamburg .	1923 <sup>1</sup> / <sub>2</sub>	„			
„ New York .	351	„			
„ Asiatic ports	225	„			
Total	6239 <sup>7</sup> / <sub>12</sub>	cases			
against	2259 <sup>5</sup> / <sub>12</sub>	„	in the same period	1905/6	
and	1881 <sup>1</sup> / <sub>2</sub>	„	„ „ „ „	1904/5.	

<sup>1)</sup> Report April 1907, 62.

<sup>2)</sup> La Revue de Grasse 50 (1907), Nr. 31.

<sup>3)</sup> Report April 1907, 62.



Linaloe-tree (*Copal limon*) in winter.



The shipments have consequently more than trebled during the last two years.

Although the reports have now for some weeks been somewhat firmer, we cannot believe in the prospect of an early change in the prices in an upward direction.

Of Java lemongrass oil large parcels have also come on offer, but owing to its deficient solubility this kind finds only few buyers, as long as good Cochin oil can be had in abundance. It follows that the producers will probably derive very little pleasure from this article in the present year.

**Linaloe oil.** The Hamburg importers, who still control the trade in this article, must recently have noticed that the consumers are not prepared to pay the prices asked by them, and as a consequence a certain depressed tone has come over the market which, it is hoped, will soon be followed by a change in the prices. Up to a few weeks ago, the supplies had with admirable dexterity been kept exactly proportionate to the demand, but since the notions of prices have gone beyond 17 marks, the interested parties seem to have lost all affection for this article. Cayenne linaloe oil, now as before, remains scarce.

From the reports of our representative, Mr. Carl Seyffert, travelling in Central and South America, we obtained particulars on the origin and production of Mexican linaloe oil, which have partly been confirmed and supplemented by observations made by Dr. Fernando Altamirano<sup>1)</sup>, Director of the Instituto Médico Nacional of Mexico, with whom Mr. Seyffert had repeated conferences. The most interesting parts of these reports may follow here:—

Mexican linaloe oil is obtained from the districts Oaxaca, Puebla, Guerrero, Morelos, Michoacan, down to Colima. A special centre of production is the course of the Rio Balsa, also called Rio Mescal. Of the places or municipal districts in which the distillation is carried on, may be mentioned:—

Oaxaca: Cuicatlan, Calihualac, Ingenio de la Pradera.

Puebla: Chiautla, Chila, Coacalco, San Juan del Rio, Tzicatlan, Tulzingo, Teotlalco, Jolalpa, Coctzala, Ixcamilpa, Ocotlán, Huehuepiaxtla, Axutla, Huachimantla, Atopoltitlan.

Guerrero: Olinalá (hence the original name of the oil olinaloe), Cualac, Iguala, Tepecuacuilco, Xalitla, Atzcala, Balsas, Cazalapan.

Morelos: Hacienda Calderón.

The oil is obtained from two different trees greatly resembling each other, of the species *Bursera*, viz., from the one called in Spanish *linaloe*, and from the *copal limón*. The former is

<sup>1)</sup> Comp. report of the Instituto Médico Nacional, Mexico, 1904, Jan.-- March.

now almost totally eradicated, but the latter is still largely represented. The natives distinguish three kinds according to the external appearance and odour: fine, common and caraway-linaloe. Fine linaloe has a very delicate and pleasant odour, the common kind less so, and the third resembles caraway. The wood of the *linaloe* tree is said to be more compact than that of the *copal limón*, which is characterised as more spongy. The oil which is met with in commerce, is chiefly obtained from the wood of *copal limón*. This tree, of which Mr. Seyffert unfortunately could only photograph specimens without leaves (see illustration), is very hardy and grows even in very stony soil; although it can most easily be propagated from cuttings, nobody thinks of planting it. The young trees, however, can only be made use of for oil production after about 20 years. It is said that during the last few years oil has frequently been placed on the market, which consisted of a mixture of oils obtained from the wood and from the fruit. The fruit is ripe in September, and forms fleshy, greenish to reddish berries of the size of a Spanish pea (*garbanzo*); they are sold by the *carga* (one *carga* is about  $2\frac{5}{8}$  bushels). The yield of oil from the fruit (which is distilled from July to September) amounts to 3%, and is larger than that from the best wood. The fruit is gathered by stripping it off with a crescent-shaped very sharp instrument, care being taken to damage the fleshy part of the berries as little as possible; the oil obtained in the distillation possesses a herbaceous odour, and resinifies very readily. For this reason it is not sold as such, but is mixed with the oil obtained from the wood, which keeps better. In order to increase the quantity and improve the quality of the oil, the Indians used to submit the fruit before the distillation to a kind of fermentation during which the herbaceous odour disappears, by placing the undamaged fruit in cases well covered with sacks, and keeping it thus for 3 to 4 days at a constant temperature so as to let the fruit mature(?).

The oil from the wood is best obtained from trees which are quite old — 40 to 60 years —; in the case of young trees it is endeavoured to increase the oil-content by cutting notches in the tree, upon which an increased formation of oil takes place, which may be regarded as a pathological product. The tree is treated thus, that strips 16" long and 8" wide are cut out of the bark and the wood down to a depth of 2", and running parallel, or preferably slanting to the direction of the trunk. If it is now found that the tree is a "heart", i. e., yellowish, highly aromatic wood, it can be used at once for distillation. If the tree has no "heart", it is left standing with open wounds so that it may develop "heart". With a view to this, the upper extremity of the notch is cut to a point, in order



The linaloe-oil districts in Mexico.

that the rain water may run alongside, but the lower edge is bevelled off in such manner that no foreign material can collect there which would set up decay. If, in spite of this, the wood should commence to rot, the part is at once planed off, so as to arrest the injury which otherwise would cause a cessation of the oil formation. If no interruption takes place, the change in the coloration of the wood becomes apparent already after a few days; after the lapse of a month a large portion of the previously white and soft wood has been transformed into yellowish, hard, and much more aromatic wood. The Indians were led to this operation by the observation that cut-off linaloe roots frequently contained so much oil, that it could be pressed out with the fingers, and that trees from which branches had accidentally broken off through gales, formed much oil, and had changed after many years. The operation, which has the effect of converting trees poor in oil into trees rich in oil, is carried out in April and September. The April cut is not so effective as the September one, as the individual trees in both cases only "mature" (i. e. run to sap) in the month of January. In October-November the trees drop their leaves. The distillation of the wood, for which only the trunk is used, is carried on in the most primitive manner, chiefly from December to June. The smaller distillers are partly still absolutely wild Indians who do not speak Spanish; actual factories are not yet in existence, which is probably due to the difficult conditions of life in the linaloe districts, where vermin abounds, and where among the Indians contagious diseases such as leprosy, etc. prevail. The yield of oil obtained in Mexico from the wood amounts at most to 2,5%. The production of Puebla is said to yield annually about 4000 to 5000 kilos. The oil is put up in kerosene tins containing 35 to 37 lbs., of which two are packed in a case.

Our representative had an opportunity of visiting a distilling installation (see illustration) belonging to Lino Castillo in Chiautla (Puebla), a rather large village which can be reached from Puebla in 11 hours. Whilst Puebla is situated about 7000 feet above sea level, the elevation of Chiautla is only about 1000 feet, in a very mountainous district difficult of access, with scant vegetation here and there.

The still, arranged for heating by direct fire, is, like the other parts of the apparatus, with the exception of the copper conical head, made from galvanised sheet iron; it is about 5 feet high, and has a diameter of 45 inches. At the lower part of the still an iron tube has been arranged, which is closed with a wooden plug wrapped up in banana leaves, and by means of which the water can be drawn off when the distillation is completed. The removable head which is already provided with means for cooling, is connected by two tubes with the condenser proper; pails or kerosene tins serve as receivers.

The apparatus is usually erected alongside a mountain stream, often far removed from the trees which are to be distilled. The filling with the cut up wood (the apparatus referred to above holds about 5 cwts. of chips) is so arranged, that a space of some 10 inches from the top of the still is left empty; next, so much water is added, that the wood is fairly well covered and that a space of some 7 or  $7\frac{1}{2}$  inches from the rim is still empty when the cover is put on. For stopping up the joints a coal-black clay is used, on the top of which damp cloths are laid.

6 to 7 Indians are employed for working the apparatus; of these, 4 cut up the wood in discs which are at once put in bags so as to avoid volatilisation of the oil. (One man can cut up about  $1\frac{1}{2}$  to 2 cwts. of wood daily.) One man looks after the fire, which is fed exclusively with wood from which the oil has been distilled, and one watches the progress of the distillation which lasts about 18 to 20 hours each time the still is filled.

The price paid at the still for wood in larger logs is 50 centavos (1/-) per arroba ( $25\frac{1}{2}$  lbs.).

Of the oil distilled in the presence of Mr. Seyffert, which probably originated from *Bursera aloexylon* Engl., we received a sample which had the following properties: the colour was bright yellow;  $d_{15^\circ}$  0,8836;  $n_D^{20}$  —  $10^\circ$  58';  $n_D^{20}$  1,46377; acid no. 5,6; ester no. 19,3; soluble in 1,8 and more vol. 70 per cent. alcohol.

**Milfoil Oil.** Arthur Sievers<sup>1)</sup> has on various occasions in 1904 distilled milfoil oil from *Achillea millefolium* L., and he now publishes the results obtained in the examination of these oils, giving them, along with earlier statements in literature on *Achillea* oils, in the form of a table for purposes of comparison. We reproduce here only the new results.

Oil I. Obtained from the fresh herb, which was cut in the morning, and distilled on the following day. Yield 0,234%. Deep blue;  $d_{18^\circ}$  0,876; sap. no. 37,7 = 13,2% bornyl acetate, or 10,27%  $C_{10}H_{17}OH$ ; sap. no. after acetylation 74 = 20,35% total alcohol  $C_{10}H_{17}OH$ .

Oil II. Distilled somewhat later from the entire plant; the herb had been previously dried, and had given off 57% water. Yield of oil from the dried herb 0,237%. Deep blue;  $d_{18^\circ}$  0,8935; sap. no. 29,3 = 10% bornyl acetate, or 8%  $C_{10}H_{17}OH$ ; sap. no. after acetylation 66,4 = 19,25% total alcohol  $C_{10}H_{17}OH$ .

Oil III. Distilled from fresh blossoms; this was also dark blue. In order to discover the body causing the blue coloration of the oils, Sievers saponified oil II, but the colour remained; he thereupon

<sup>1)</sup> Pharm. Review 25 (1907), 215.

distilled it, without, however, arriving at any definite result. Of acids, acetic acid was detected.

**Mustard Oil.** The methods for determining the content of allylisothiocyanate in mustard oil have already induced various authors<sup>1)</sup> to suggest modifications. Recently, C. Pleijel<sup>2)</sup> has criticised the directions given in the Swedish Pharmacopœia (VIII), and he proposes the following directions for testing, by which he has obtained, with a considerable saving in time, values which agreed very well: 5 g. mustard spirit (1 part mustard oil and 49 parts alcohol) are mixed with 50 cc.  $\frac{1}{10}$  n. silver nitrate solution and 2 cc. ammonia liquor in a well closed standard flask of 100 cc. capacity. The flask with its contents is then heated for 3 hours to a temperature of 45 to 50°, but is every half hour shaken for half a minute. When the mixture has cooled, 5 cc. nitric acid, 1 cc. iron alum solution, and so much water are added, that the total volume amounts to 100 cc.; it is then shaken, and filtered through a dry filter. In 50 cc. of the filtrate the quantity of silver solution which has not entered into reaction is then determined by titration with  $\frac{1}{10}$  n. ammonium rhodanide solution.

**Myrtle Oil.** The alcohol myrtenol discovered some time ago by v. Soden and Elze<sup>3)</sup> in myrtle oil, has been examined more in detail by Semmler and Bartelt<sup>4)</sup>. In order to obtain it, the high-boiling portions of myrtle oil were saponified and then fractionated, and the alcohol isolated by means of the phthalic acid compound (m. p. 114 to 115°;  $[\alpha]_D + 21^\circ 36'$  in 50 per cent. alcoholic solution). It has the composition  $C_{10}H_{16}O$ , and possesses the following properties: b. p. 102,5° at 9 mm. pressure, 222 to 224° at atmospheric pressure;  $d_{20^\circ} 0,9763$ ;  $\alpha_D + 45^\circ 45'$ ;  $n_D 1,49668$ ; mol. refraction found 45,46, calculated for  $C_{10}H_{16}O/\bar{45,04}$ . From the molecular refraction the authors conclude that myrtenol has a bicyclic character. A solid phenyl urethane could not be obtained. When treating myrtenol with sodium and amyl alcohol, it remained unchanged. By means of phosphorus pentachloride the chloride  $C_{10}H_{15}Cl$  was obtained (b. p. 90° at 12 mm. pressure;  $d_{20^\circ} 1,015$ ;  $\alpha_D + 24^\circ$ ;  $n_D 1,49762$ ; mol. refr. found 49,2, calculated for  $C_{10}H_{15}Cl/\bar{48,48}$ ), which on reduction with alcohol and sodium yielded, besides myrtenol ethyl ether  $C_{10}H_{15}OC_2H_5$  (b. p. 80 to 85° at 10 mm. pressure;  $d_{20^\circ} 0,899$ ;  $n_D 1,4725$ ), dextro-rotatory pinene of the following properties: b. p. 155 to 158°;  $d_{20^\circ} 0,862$ ;  $\alpha_D + 28^\circ$ ;  $n_D 1,4695$ ; mol. refr. found 44,02, calculated for  $C_{10}H_{16}/\bar{43,52}$ . The identity with pinene could be proved

1) Comp. Reports April 1904, 63; October 1904, 59; April 1906, 45.

2) Farmac. Revy 1907, 204, acc. to Apotheker Ztg. 22 (1907), 521.

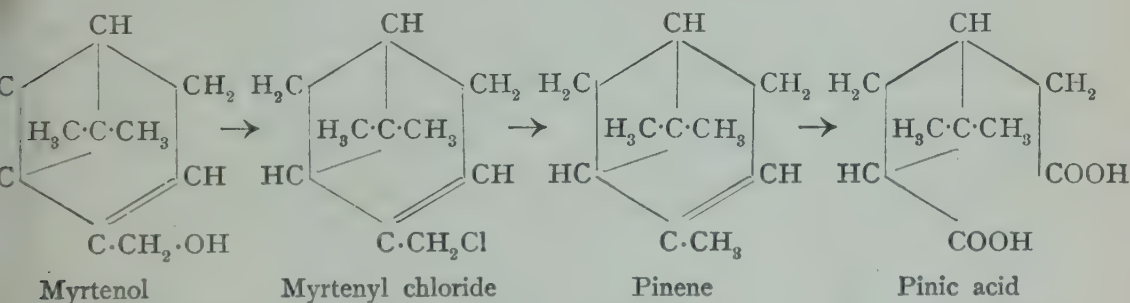
3) Chem. Ztg. 29 (1905), 1031; Report April 1906, 47.

4) Berl. Berichte 40 (1907), 1363.

by the well-known derivatives. The high optical rotation calls for attention.

By oxidising myrtenol with chromic acid in solution of glacial acetic acid, the aldehyde myrtenal  $C_{10}H_{14}O$  was obtained (b. p.  $87$  to  $90^{\circ}$  at 10 mm. pressure;  $d_{20}^{\circ}$  0,9876;  $n_D$  1,50420; mol. refr. found 44,96, calculated for  $C_{10}H_{14}O$   $\sqrt{43,79}$ ; semicarbazone m. p. about  $230^{\circ}$ ), which could be converted over the oxime (m. p.  $71$  to  $72^{\circ}$ ) and the nitrile, in to myrtenic acid  $C_{10}H_{14}O_2$  (m. p.  $54^{\circ}$ ). From the properties of the methyl ester of this acid, (b. p.  $99^{\circ}$  at 9 mm. pressure;  $d_{20}^{\circ}$  1,022;  $n_D$  1,48616; mol. refr. found 50,55, calculated for  $C_{11}H_{16}O_2$   $\sqrt{49,84}$ ), Semmler and Bartelt draw the conclusion that it still belongs to the bicyclic, singly unsaturated system of myrtenol. This view is supported by the fact that it was possible to produce from the ester by reduction with sodium and amyl alcohol, a hydrated myrtenic acid  $C_{10}H_{16}O_2$  (b. p.  $142$  to  $144^{\circ}$  at 8 mm. pressure;  $d_{20}^{\circ}$  1,049;  $n_D$  1,48519; mol. refr. found 45,9, calculated for  $C_{10}H_{16}O_2$  45,7) which behaved like a saturated bicyclic acid. Whilst the experiments mentioned up to the present showed that myrtenol is a primary alcohol, possessing the carbon structure of pinene, the oxidation of myrtenol with permanganate into pinic acid showed the position of the  $CH_2 \cdot OH$ -group (see formula). When boiled with 10 per cent. sulphuric acid, myrtenol yielded a hydrocarbon  $C_{10}H_{14}$  (b. p.  $55^{\circ}$  at 9 mm. pressure;  $d_{20}^{\circ}$  0,858;  $n_D$  1,49097;  $n_D \pm 0^{\circ}$ ) which is possibly cymene.

On the strength of the facts communicated above, Semmler and Bartelt draw up the following formulæ for myrtenol and its products of conversion:—



**Oil of Nardostachys Jatamansi (?).** From the drug *Kansho-ko*, which is popular in Japan as a perfume, and which is probably the rhizome with attached rests of leaves of *Nardostachys Jatamansi* D. C. (Valerianaceæ), Y. Asahina<sup>1)</sup> isolated 1,9% of a greenish yellow pleasantly smelling oil, which readily resinifies on exposure to the air;  $d_{15}^{\circ}$  0,9536;  $[\alpha]_D$  —  $11^{\circ}30'$ ;  $n_D^{80}$  1,571; acid no. 0; sap. no. 45,7; sap. no. after acetylation 66,42. The oil contains a sesquiterpene boiling at  $250$  to  $254^{\circ}$  ( $d_{15}^{\circ}$  0,932).

<sup>1)</sup> Journ. of the pharm. Soc. of Japan 1907, 355.

**Neroli Oil.** The severe cold of the past winter appears to have only had a retarding effect on the orange blossom harvest, for the result of about 1900000 kilos, which has been obtained according to various estimates, falls but little short of the results of a normal harvest. Of the above quantity, about 1200000 kilos belong to the Syndicate; the average price paid this year for the blossoms was about 1,20 francs per kilo. Many complaints have been heard about the yield of oil, as during the distillation the weather was mostly cool and rainy. The oil prices moved at first between 700 and 750 francs per kilo, but soon advanced to 800 francs, as an exceptionally brisk demand arose and stocks of last year's harvest could not be reckoned upon. A few producers ask already 900 francs per kilo, but do not appear to be able to arouse much interest at that figure on the part of the consumers.

The scarcity of oil last year has induced a large number of consumers to turn their attention to our artificial neroli oil, and the expectations to which we gave expression in our Report of October 1906 have been fulfilled in every respect. Many of our friends have adopted the exclusive use of our artificial product, the advantages of which must be obvious to every interested person.

**Nutmeg Oil.** Although the commercial value of nutmegs has fallen considerably in recent times, the cultivation of the trees<sup>1)</sup> is still of sufficient importance. In the forests of India several species occur in the wild state, especially *Myristica longifolia* (Syn. *M. coriicosa*) and *Myristica attenuata*; but *Myristica fragrans* supplies the product of commerce. This latter species is also the only one cultivated; it was introduced by the Dutch in Ceylon, and thence brought to India. The tree develops in a moist, warm climate, and requires a fertile soil. Apart from the care which every culture requires, and the expenses of laying out the plantation, the nutmeg tree causes but very little trouble. 7 to 10 years after planting, the trees blossom and bear fruit; they are able to yield crops for a very long time. On an average, one tree yields annually about 200 nutmegs.

**Orris Oil.** The present position of the orris root market is described by our correspondents as follows:—

Since the date of our Spring report, no pronounced changes have taken place in the prices of Florentine orris root, as to-day 68/70 marks cif. Hamburg must still be paid for assorted roots, and 60/62 for seconds. As to the quality, however, it is to be regretted that a step in the backward direction has again to be recorded. Excepting a few small parcels, the roots of the new harvest which have been brought in are lean and stunted throughout; the fine full roots of former times are totally absent, and it is easy to recognise from the article the consequences of the severe drought and the neglect of the cultivation.

<sup>1)</sup> Annales de Pharmacie 13 (1907), 189.

In order to produce choice qualities, it is therefore necessary to fall back upon old roots which under the conditions described can only be had at high prices. But this quantitative result of the harvest will also be affected by the failure of the roots, so that some of the estimates are very low — in our opinion probably too pessimistic; for the present we are rather inclined to stand by our previous estimate of about 500 tons, as goods are frequently still brought in up to the beginning of November.

At the end of February 1907 there were available . . . about 680 tons  
Deduct from this the shipments from the beginning of March  
to the end of August . . . . . „ 140 „

There remains a balance on 1<sup>st</sup> September 1907 of . . . about 540 tons.

It will be seen that the export in the half-year March/August was very small in comparison with the same period of last year, when it amounted to 370 tons, but it is said that fairly large parcels have still to be shipped against earlier contracts.

Altogether there were shipped during the last 12 months:—

September 1906/August 1907 about 550 tons					
against	„	1905/	„	1906	„ 920 „
	„	1904/	„	1905	„ 500 „
	„	1903/	„	1904	„ 820 „
	„	1902/	„	1903	„ 840 „

Basing upon the harvest estimates, which fluctuate between 300 and 500 tons, and taking into consideration the old stocks in hand (540 tons), we arrive at a total available quantity of 840 to 1040 tons for the season September 1907 to August 1908, so that with an annual export as hitherto observed, a sufficient supply would be available. But a fact which may undoubtedly affect the prices of Florentine orris root is the prospective extremely small crop in the Veronese district, inasmuch as the Veronese orris harvest next due is estimated at most at 60 to 80 tons, against a previous maximum of about 600 tons. It should also be mentioned that the new quantities planted out during the last two years have been moderate, in spite of the rise in the prices, — no doubt a salutary consequence of previous sorry experience — and for this reason no exceptionally large crops can be expected for the next few years.

The movements in the prices during the past twelve months were of no importance, and as regards the future, it is possible that in consequence of last year's feeble export, the demand from abroad during the new season may be all the greater, in which case the market might easily become firmer.

**Patchouli Oil.** In spite of large sales in this important article, the European market has not yet been able to meet the increased prices of the raw material by an advance in the prices of the oil, and all symptoms point to the fact that everywhere abundant quantities of distillate of low cost-price are still available. Of the Indian distillate, which is useless for the purposes of the fine perfumery, there exist everywhere important stocks which can only be disposed of at a loss. It is to be hoped that the producers may be induced by their bad experience to restrict their manufacture in due proportion. The prices of the leaves, which reached their highest level in April with 40/- per cwt., have meanwhile fallen to 36/-, but there does not appear to be any prospect of a further decline of the market to the previous level of 26/-, as the cultivation is said to have suffered greatly from heavy rainfall.

**Oil of European Pennyroyal.** The scarcity of oil of European Pennyroyal, which had existed since last year, has become somewhat less pronounced by the arrival of the new Spanish distillate, but the supply does not yet seem to equal the demand, and the prices show as yet little inclination to return to their previous level. A few large parcels which were recently sold had to be rejected on account of defective quality. Of Algerian oil, very little comes on offer.

The prices of American pennyroyal oil (being consumed chiefly in the United States) reached the respectable height of 3.25 dollars per lb., which must be paid whether the purchaser likes it or not. Owing to the brisk demand, with very limited stocks, the distillation was commenced very early this year, and the bulk of the material was worked up in the undeveloped state. Whilst formerly North Carolina supplied most of the pennyroyal oil, the industry now also receives great attention in the State of Tennessee.

The constituents of the oil of American pennyroyal (*Hedeoma pulegioides* L.) have been examined more in detail by Marmaduke Barrowcliff<sup>1)</sup>. The oil, supplied by Fritzsche Brothers, of New York, had the following constants;  $d_{15}^0$  0.9297;  $n_D^{20}$   $+25^{\circ}44'$ ; soluble in 2 vol. 70 per cent. alcohol. Of free acids there were detected in the oil, formic, butyric, octylic, and decylic acids. By extraction with 5 per cent. caustic potash liquor, Barrowcliff obtained small quantities of a not further examined phenol, and also traces of salicylic acid, which was probably present in the oil in the form of the methyl ester. From the portions of the oil boiling above  $120^{\circ}$  (60 mm.), pulegone (24.1% of the oil) was isolated by bisulphite solution, and identified by the melting point of the semicarbazone ( $171^{\circ}$ ). The portion treated with bisulphite was saponified, the oil obtained was distilled at 60 mm., and then distilled at ordinary pressure jointly with the portions boiling below  $120^{\circ}$  (60 mm.) of the oil extracted with soda solution and caustic potash liquor. In the fraction of 155 to  $165^{\circ}$  thus obtained were detected small quantities of l-pinene, in the fraction passing over at 165 to  $170^{\circ}$  1-methyl-3-cyclohexanone (8%) which after regeneration from the semicarbazone (m. p.  $182$  to  $183^{\circ}$ ) distilled at 167 to  $168^{\circ}$ ; this appears to be the first time that the presence of this ketone has been observed in nature. The same fraction and also the next fraction of 170 to  $180^{\circ}$ , contained small quantities of l-limonene and dipentene.

After small quantities of pulegone had still been worked out from the fraction passing over at 212 to  $217^{\circ}$ , the purified fraction was employed for producing semicarbazones, when it was found possible

<sup>1)</sup> Journ. chem. Soc. **91** (1907), 875.

to obtain two bodies which by their melting points,  $184$  to  $186^{\circ}$  and  $125$  to  $126^{\circ}$  respectively, proved to be those of l-menthone and d-menthone (total  $50\%$  of the oil). The l-menthone, regenerated from the semicarbazone boiled at  $207$  to  $208^{\circ}$  (m. p. of the corresponding oxime  $58$  to  $59^{\circ}$ ); the other regenerated ketone with the opposite rotation boiled at  $209$  to  $210^{\circ}$  (its oxime was oily). This menthone proved to be identical with the dextrorotatory constituent found by Beckmann in inverted menthone, and according to Aschans nomenclature must be termed d-isomenthone. The fraction passing over from  $300$  to  $310^{\circ}$  contains a sesquiterpene alcohol ( $2\%$ ), from which was obtained a sesquiterpene with the following properties:  $d_{20} 0.8981$ ;  $\alpha_D + 1^{\circ} 4'$ ;  $n_{D20} 1.5001$ ; b. p.  $270$  to  $280^{\circ}$ ; mol. refr.  $66.8$ . Of combined acids Barrowcliff found, besides salicylic acid already stated, also formic, acetic, octylic, and decylic acids, and a non-volatile dibasic acid of the formula  $C_8H_{14}O_4$  (m. p.  $83$  to  $85^{\circ}$ ).

**Peppermint Oil, American.** Our New York branch has this year again, as usual, despatched an expert to the producing districts of the States of New York, Michigan, and Indiana, and from his report we abstract the following data:—

#### I. Wayne County, New York.

The weather has been very unfavourable since the beginning of the spring, as practically no rain has fallen, and as the drought also continued in the time which is most important for the development of the plants, i. e., in August, the whole of the peppermint cultivation has suffered to a not inconsiderable extent. The area covered with last year's and this year's plants, amounts to the following:—

	last year's	this year's
Williamson	4 acres	$2\frac{1}{2}$ acres
Marion	$25\frac{1}{2}$ "	24 "
Palmyra	21 "	16 "
Sodus	38 "	$22\frac{1}{2}$ "
Arcadia	131 "	$109\frac{1}{2}$ "
Junius	12 "	9 "
Galen	12 "	8 "
Rose	5 "	5 "
Lyons	$118\frac{1}{2}$ "	71 "
Phelps	7 "	$4\frac{1}{2}$ "
	<hr/> 374 $\frac{1}{2}$ acres	<hr/> 272 acres
	Total 646 $\frac{1}{2}$ acres.	

The prospective yield of oil is estimated at 10 lbs. per acre for last year's, and 35 lbs. per acre for this year's peppermint. This would therefore give the following result:—

3745 lbs. from last year's plants
9520 „ „ this „ „
<hr/> Total 13265 lbs.

The stocks of oil of the 1905 and 1906 productions still in the hands of the producers are estimated this time exceptionally high; no less than 15000 lbs., that is to say more than the expected yield of this year's harvest, are said to be still available. The falling prices of last season had clearly induced the farmers, who were almost throughout in good circumstances, to hold back their production in anticipation of a change in the prices, but as already reported by us in April, their hopes have not been realised, owing to the movement of the market.

## II. Michigan and Indiana.

In consequence of the unfavourable weather, the distillation begins this year about four weeks later than usual, and owing to this it was very difficult at the time of the visit of our correspondent (end of August), to form an opinion as to the probable result. In consequence of the delay, the second cut will not take place until the middle of October, and with the abnormal weather conditions it must be feared that by that time frosts will occur, and will cause a certain amount of damage.

The following areas are under cultivation:—

Michigan: Berrien Co.	540 acres	
St. Joseph Co.	935 „	
Eaton Co.	310 „	
Branch Co.	365 „	
Kalamazoo Co.	524 „	
Van Buren Co.	936 „	
Allegan Co.	1660 „	
Muskegan Co.	720 „	
Various	500 „	6490 acres
Indiana: South Bend	262 acres	
Mishawaka	849 „	1111 „
	<hr/> Total	7601 acres.

The prospective yield of oil is estimated in Michigan at an average of only about 17 lbs., but in Indiana at about 33 lbs. per acre, so that the oil yield might probably come to

about 110330 lbs. in Michigan
„ 36663 „ „ Indiana
<hr/> total about 146993 lbs.

For the reason already stated, these figures can only be given with reserve as representing the actual result of the harvest. Of last season, it is said that no less than 60000 lbs. (!) which were held back in expectation of better prices, are still unsold in the hands of producers.

If the estimates for the three districts are taken together, we obtain the following summary of the quantities available for the new season:—

New York . . . . .	about	28 000 lbs.
Michigan and Indiana . . . .	„	<u>205 000 „</u>
Total		233 000 lbs.

The tone is everywhere very weak, and as moreover no stimulation may be looked for from the Japanese peppermint oil market, an improvement in the prices in the near future cannot be reckoned upon.

We would still add that the Essential Oil Department of the American Society of Equity, to which we referred in our last October Report, has ceased to exist; from this it would appear that this movement has found little support from the side of the interested parties.

**Peppermint Oil, English.** Owing to the cold weather in the months of April and May, the growth of the plants has been retarded very considerably, and not until the end of August it was possible to form an at least somewhat reliable opinion on the prospects of the harvest. Unfortunately, the hopes built upon the influence of the change in the weather in June have not been realised, for, although the herb has generally thriven extremely well, the small yield of oil, probably due to the large amount of moisture during the summer months, is generally complained about. Moreover, a large number of fields had to be cleared prematurely, as the plants had been attacked by a fungus-disease which threatened to destroy them. The general opinion is that this year's crop only amounts to about  $\frac{2}{3}$  of last year's, and that consequently the total result must be characterised as semi-normal. Naturally the prices have experienced a proportionate upward movement, and now fluctuate between 34/- and 36/- per lb., equal to a quotation of nearly 80 marks for rectified oil. As we only have at our disposal a medium quantity of old stock, we shall soon have to adjust our prices in complete harmony with the upward movement. How the consumers will face this surprise must be awaited, but no doubt the demand will then turn more towards the American oil which can be had very advantageously this year.

**Peppermint Oil, Japanese.** The information in our April Report, which questioned the legitimacy of the Japanese expectations of higher prices for their peppermint products, has been confirmed by

the occurrences of the last six months, for in spite of the obstinate resistance of the producers, the quotations of the oil have since that time declined without intermission. This downward movement of the market would doubtless have proceeded more rapidly if not large stocks at high cost-prices had been held in Europe and America, the holders of which also used every possible effort to protect themselves against the prejudicial effects of the downward movement. Finally, the holders, in face of the approaching harvest, and not the least on account of the stringency of the money market, were forced to realise, and the prices gradually fell to their present level. This, however, has not taken place without some temporary reactions.

There are three different estimates of the approaching harvest, which show the following figures:—

	I.	II.	III.
Hokkaido	about 170000 kin	abt. 120000 kin	abt. 150000 kin
Yamagata	„ 20000 „	„ 25000 „	„ 20000 „
Bingo Bitchiu	„ 100000 „	„ 80000 „	„ 100000 „
	about 290000 kin	abt. 225000 kin	abt. 270000 kin
	or an average of about 260000 kin.		

To this must be added about 60000 kin stocks at various places in the interior, and also about 100000 kin oil unsold in the hands of the refiners, so that a total of about 420000 kin may possibly be available for consumption, against about 275000 kin in 1906<sup>1)</sup> and about 430000 kin in 1905. Although the final result of the harvest will naturally depend above all upon the weather during the next few months, it may in our opinion be assumed from these figures that, if no unforeseen circumstances upset human calculation, the prospect of a hardening of the quotations is for the present very small indeed.

According to our correspondents, the cultivation in the Province of Bingo Bitchiu is smaller this year than in 1906, which must be attributed to the fact that the price of rice has advanced to an unexpected height. This has induced many farmers to plant rice, and give up the cultivation of peppermint. On the other hand, in Hokkaido a somewhat larger area is said to be planted with peppermint.

From the Report of the German Consul at Kobe<sup>2)</sup> we abstract the following information regarding Japan's trade in menthol and peppermint oil:—

The export of these two articles, which up to the present had taken place almost exclusively via Yokohama, is now also finding its

<sup>1)</sup> According to another estimate, only 241000 kin.

<sup>2)</sup> Berichte über Handel und Industrie 10 (1907), 608.

way via Kobe; the share of this port increased from 11% of the total exports in 1900 (25705 out of 223471 yen) to nearly 47% in 1906 (422575 out of 888693 yen). The oil distilled on the spot by a simple process enters the refining works in an impure condition and is there separated into crystals and oil. The yield of menthol fluctuates according to the different harvests; the first cut (July to August) yields about 35 to 40%, the September cut 40 to 50%, the third (up to the end of October) 50 to 60% crystals. The rests consists of the so-called "pure oil", which still contains about 10% menthol. Two refineries are situated in Kobe, one of which has been established with German money. The principal article in Kobe is the brand of the Suzuki refining works.

In the country itself neither menthol nor oil are much used, the bulk being exported. The following table abstracted from the Customs' statistics gives particulars of the movement of the trade during the last 5 years:—

### Menthol crystals.

					Of the total exports were shipped to:				
					Of which export- ed via Kobe				
	Quantity kin	Value yen	Quantity kin	Value yen	Hong- kong kin	The United Kingdom kin	Ger- many kin	Ame- rica kin	Ma- nila kin
1902	54332	463718	591	6154	15487	10524	7744	14861	15
1903	76851	804401	29694	296695	21123	15533	18718	15307	61
1904	144148	1090742	42255	337325	21882	33686	19400	47789	8
1905	167067	797624	48789	234718	13476	63949	24417	30656	31
1906	95549	517215	37139	205196	(Not yet known.)				

### Peppermint oil.

					Of the total exports were shipped to:				
					Of which export- ed via Kobe				
	Quantity kin	Value yen	Quantity kin	Value yen	Hong- kong kin	The United Kingdom kin	Ger- many kin	Ame- rica kin	Ma- nila kin
1902	59240	164864	9457	40062	22962	12832	14874	4190	15
1903	77024	277616	35916	120281	24584	15392	24230	7125	5
1904	174769	558949	86893	282516	53382	40540	25816	24490	16
1905	173906	491590	87050	249452	43640	58370	37868	18536	15
1906	121138	371478	69969	217386	(Not yet known.)				

The decrease in the exports of the year 1906 is explained thus, that the consumers had laid in abundant supplies at the time of the good harvest in the previous year, and consequently did not buy so much new oil. The yield of natural (unseparated) oil during the last

two years showed the following figures, including the production in the North: —

	1905	1906
First cut . . . . .	20 000 kin	6 000 kin
Second cut . . . . .	70 000 „	40 000 „
Third cut . . . . .	50 000 „	35 000 „
Total yield in the North (Yokohama) . . . . .	90 000 „	80 000 „
	<hr/> 230 000 kin	<hr/> 161 000 kin
Add old stocks . . . . .	200 000 „	80 000 „
Grand total, available for export . . . . .	430 000 kin	241 000 kin

A further table illustrates the considerable fluctuations in the prices on the peppermint market, which, for the rest, are also a peculiarity of other Japanese products.

**Peppermint Oil, French.** The cultivation of mint, which in France had long been confined to the Grasse district, has always been one of the more important industrial enterprises of France. In recent years it has also extended to the valley of the Var, up to Entreveaux. In order to keep the cultivation at a remunerative level even with a possible fall in the prices, a rational method of fertilisation must be observed in the cultivation of mint, a matter to which up to the present not sufficient value has been attached. L. Belle<sup>1)</sup> reports, in a long article on the experiments made with various kinds of manure.

In Villeneuve-Loubet, the most important place for the mint-cultivation, in the Sea-Alps, and where up to the present the comparatively largest crops have been obtained, the manure generally used consists of sesame oil cakes, and that in the enormous quantity of 5 to 6 tons per hectare ( $2\frac{1}{2}$  acres), which gives rise to an expenditure of about 750 to 900 francs; and the farmers do not trouble whether or not this method is really a rational one. According to analyses by Charabot and Hébert, mint contains during its entire vegetation-period 0,25% nitrogen, 0,146% phosphoric acid, and 0,794% potash. A crop of 30 000 kilos, which is not infrequently obtained in Villeneuve-Loubet, would correspond to 73,5 kilos nitrogen, 43,8 kilos phosphoric acid, and 238,2 kilos potash. With a fertilising agent such as sesame oil cakes, which contain on the average 6% nitrogen, 2% phosphoric acid, and 1% potash, there would be given to the soil, if 6000 kilos are used, 360 kilos nitrogen, 120 kilos phosphoric acid, and 60 kilos potash. Consequently the necessary fertilisers, with the exception of phosphoric acid, are given in the reverse proportion, if the analytical results are taken into consideration. When this fertiliser is employed,

<sup>1)</sup> Journ. de la Parfumerie et Savonnerie Françaises 20 (1907), 80.

nitrogen is squandered (apart from the unnecessary expense), and in spite of this, a good crop can only then be reckoned upon, in view of the large quantity of potash required by mint, if the soil is extraordinarily rich in potash, a fact which has been confirmed by Belle's experiments. These experiments showed that mint requires a very abundant fertilisation which at the same time must be capable of ready assimilation, owing to the great demand of this plant for fertilisers, and its rapid growth; for this reason the nitrogen is best added to the fertiliser in the form of anorganic compounds, rather than in organic form. For normal soils Belle recommends, in view of his experiments, the following fertilisation: 20000 kilos stable manure, 300 kilos Chili saltpetre, 400 kilos superphosphate, and 300 kilos potassium sulphate; or 1500 kilos sesame oil cakes, 300 kilos Chili saltpetre, 400 kilos superphosphate, and 500 kilos potassium sulphate per hectare. The Chili saltpetre is best distributed in two portions, two thirds when planting the mint (at the end of February or the beginning of March), and one third about the middle of May. For the rest, the Chili saltpetre can be replaced by ammonium sulphate, of which a quantity of 225 kilos is put into the soil immediately on planting. The superphosphate and the potassium sulphate are spread at the same time as the stable manure.

4 **Petitgrain Oil.** We are unfortunately not yet in a position to announce to our friends the prospect of an approach of improved conditions for this article, for the supplies are now as before so short, that they are mostly absorbed by contracts made at earlier dates. From the producing district it is reported that the bad state of affairs is growing worse, for the forests have recently been attacked by a devastating plague of locusts, so that it is necessary to remove the manufactories to other districts. This shows that the production is meeting with an increasing number of obstacles.

**Pilea Oil.** In our Reports (October 1906, 83 and April 1907, 105) we recently described as a novelty pilea oil, in which we had detected a small quantity of pinene, whilst the principal constituent of the oil had not yet been discovered. Professor Semmler<sup>1)</sup>, at whose disposal we placed the oil for the purpose of further examination, now states in a short publication that he has found in the fraction of the b. p. 167 to 168°, representing the bulk of pilea oil, sabinene ( $d_{20}^0$  0,8402;  $n_D + 61^\circ 20'$ ;  $n_D$  1,46954). The identity with sabinene was seen from the formation of sabinene glycol (b. p. 150 to 154° at 9 mm. pressure;  $d_{20}^0$  1,0332;  $n_D$  1,48519; molecular refraction found 47,17, calculated for  $C_{10}H_{18}O_2$  46,97) on oxidation

<sup>1)</sup> Berl. Berichte 40 (1907), 2963.

of the above-mentioned fraction with potassium permanganate. At a later date a detailed report on pilea oil shall be issued.

**Pine needle Oils.** Up to the present it has, unfortunately, not yet been possible to meet definitely the scarcity of oil from pine cones, as we have hitherto only received unimportant quantities of the fresh distillate. The producing district in the West of Switzerland has, according to our correspondents, suffered considerably from the unfavourable weather conditions, so that this year's distillation-result will probably only come to half the production of previous years. Towards the end of the month we hope to receive further small supplies. The other kinds, the oils from *Abies alba*, and *Pinus montana*, and also Siberian pine needle oil, were available in abundant quantities, and especially the latter has become introduced in the most diverse branches of industry, on account of its low price and its exceptional usefulness.

In continuing his work on the constituents of Siberian pine needle oil<sup>1)</sup>, Schindelmeiser<sup>2)</sup> has recently succeeded in demonstrating definitely, in a fraction of the b. p. 175 to 182°,  $\alpha_D - 14^\circ 31'$ , the presence of dipentene, (which at the time was not detected with certainty) by means of the production of the dihydrochloride and dihydrobromide (m. p. 49 and 64° respectively) and of the tetrabromide (m. p. 154°; probably a printer's error, instead of 124°?). The constants of the terpene were: b. p. 176 to 178°;  $d_{20} 0.847$ ;  $\alpha_D \pm 0$ ;  $n_D 1.47312$ . The presence of d-phellandrene in this oil could also be proved, inasmuch as from the fraction of the b. p. 169 to 172° ( $\alpha_D - 17^\circ 20'$ ) containing dipentene, a crystalline nitrite of the m. p. 106 to 107° was formed. Its rotation, in 4.34 per cent. chloroform solution, ( $d_{20} 1.478$ ) was  $[\alpha]_D - 46.16^\circ$ .

The total weight of the crude dipentene and phellandrene fractions together equalled 5.4% of the oil.

**Oil of Pinus Sabiniana** Douglas. The results of the examinations of this oil mentioned in our last Reports<sup>3)</sup> are confirmed by a work by Frank Rabak<sup>4)</sup> who, like ourselves, used as crude material a balsam supplied by Green & Co., Oroville, Cal. The alcoholic solution of the semi-solid, dirty brown balsam, was optically inactive; it had as acid no. 127; ester no. 37; sap. no. 164. By means of distillation with steam, 7.3% of a colourless essential oil with a pleasant odour like oranges were obtained from the

<sup>1)</sup> Apoth. Ztg. **19** (1904), 815. Report April **1905**, 65.

<sup>2)</sup> Chem. Ztg. **31** (1907), 759.

<sup>3)</sup> Report October **1906**, 64; April **1907**, 85.

<sup>4)</sup> Pharm. Review **25** (1907), 212.

balsam:  $d_{230} 0,677$ ;  $\alpha_D \pm 0^\circ$ ; soluble in 3 vol. 95 per cent. alcohol, but slightly soluble in dilute (50 per cent.) alcohol. The principal constituent of the oil was found to be heptane (formerly abietene), which also agrees with the result  $d_{230} 0,677$  and b. p. 100 to 101°. Pinene could not be detected with certainty in the oil. Towards the end of the steam-distillation, a small quantity of a yellowish oil ( $d_{230} 0,810$ ) passed over, which could not be examined further. By extraction of the bulk of the distillate with 50 per cent. alcohol, Rabak isolated the readily soluble characteristic bearer of the odour of the oil as a golden-yellow oil; its 10 per cent. alcoholic solution was optically inactive; acid no. 42; ester no. 124; sap. no. 166. The alcohol isolated in the form of a yellowish oil from the saponified oil could not be identified further owing to scarcity of material.

In the distillation-water, which was obtained from the balsam when driving the oil off, acetic acid and formic acid were detected. The resin remaining behind as distillation-residue was transparent, hard, and brittle; its alcoholic solution was optically inactive, its acid no. 142; Rabak was, however, unable to isolate crystals of abietic acid from the resin. —

**Rose Oil, Bulgarian.** As could only be expected after the exceptionally severe winter, the result is this year considerably smaller than in 1906; the shortage is almost throughout estimated at about 45%. The total production is said to be 2513 kilos, against 4600 kilos last year. It is divided over the individual districts as follows: —

Kazanlik . . . .	874 kilos
Nova-Zagora . . . .	85 „
Stara-Zagora . . . .	115 „
Tchirpan . . . .	190 „
Philippople . . . .	319 „
Petchera . . . .	64 „
Panagurishtë . . . .	7 „
Karlovo . . . .	859 „

Total 2513 kilos.

We are informed that the rose-bushes this year were almost a whole month behind in their development, as unfavourable and cold weather had retarded the growth. Whereas in 1906 roses flowered as early as April 30, it was this time only possible to commence operations towards the end of May. At the time of the distillation itself, the weather generally was very satisfactory, which found its expression in many places in a decidedly higher yield of oil than in the previous year. In view of the considerable shortage, higher prices than in 1906 would of course have been justified right from the first, and the yearly

returning farce of the fixing of the prices would have been carried through quicker, and in a simpler manner, if there had not been voices predicting lower prices on the supposition that considerable stocks of old oil were still in the hands of merchants. So far as we have been able to ascertain, this view is solely represented by the correspondent of *The Chemist and Druggist*, and the expression of his views<sup>1)</sup> has called forth an amount of public and private commentary, which ascribes to him the most varied motives. We must refrain from going further into this question, the more so, as to us also the situation does not yet seem sufficiently clear to say definitely which of the two parties is right.

In any case the prices of first quality oil in the producing country have gradually advanced to the parity of 775 marks per kilo, and in spite of the rumours of lower rates they appear to maintain themselves at that level. We would still point out that we have never before received so many adulterated samples for testing as this year, and we consider it our duty to call once more the attention of our friends to the fact that our testing laboratory, the services of which are at the disposal of our clients without charge, possesses exceptional experience in judging this article.

The foregoing agrees on all essential points with the Report of the German Consul at Constantinople, which may follow here *in extenso*:

The very severe winter, and the exceptionally rough spring with the subsequent continuous drought, have had an extraordinary retarding effect on the development of the rose gardens. The cooler weather with copious rainfall which prevailed later on and also during the distilling season, came unfortunately in many instances too late. The bushes were no longer able to bud afresh, only the buds already in existence were saved from drying up. The distillation was also delayed owing to the unusual weather-conditions, and could only at the end of June be said to have come to a conclusion.

The estimates of the total result fluctuate between 450 000 and 600 000 meticals. If the former figure is taken as a basis, only 2100 kilos rose oil would have been harvested, i. e., about 40% less than last year when the harvest amounted to about 3600 kilos.

The demand is accordingly very considerable. In Bulgaria the few old parcels still in stock (including oils two and three years old) have been bought up at high prices. The price of finest unadulterated Bulgarian rose oil is to-day 750 marks per kilo, and is still moving upwards.

**Rose Oil, French.** According to an article in *La vie à la Campagne*<sup>2)</sup>, which has also appeared in *La Revue de Grasse*<sup>3)</sup>, efforts are now made in the South of France to render the rose cultivation there more productive, so as not to be, as hitherto, almost exclusively dependent upon the Bulgarian oil production.

<sup>1)</sup> *Chemist and Druggist* 71 (1907), 64, 97 and 196.

<sup>2)</sup> *La Vie à la Campagne* 1 (1907), 414.

<sup>3)</sup> *La Revue de Grasse* 1907, No. 13.

The species of rose mostly cultivated at the moment in Southern France, is *Rosa damascena* Mill., of which a local variety *la Muscadine* is particularly popular. In addition to these, there are also cultivated the *Rose de Provins*, a form of *Rosa gallica*, and *Rosa centifolia* L. They are chiefly worked up for rose water, and rose oil is only obtained thereby as a by-product, and is consequently of no importance for the trade.

The distillation is carried on thus: 50 kilos flowers are added to 300 litres water, and from this 100 litres rose water (value 60 francs) are distilled off. The quantity of oil obtained in this process (which oil is said to be of a distinctly finer quality than the Bulgarian oil) amounts to at most 1 gram (= 2 francs). In the two departments Alpes-Maritimes and Var, about 1500 acres are cultivated with roses, the yield per acre being about 1200 kilos, making a total of 1800000 kilos rose blossoms. Based upon the above yields, the production of rose oil is 36 kilos, and that of rose water 3600000 litres, of a total value of 2232000 francs. Besides this distillation process, which is almost universally employed in the South of France, here and there the system of enfleurage (with paraffin), and the extraction of the blossoms with petroleum ether or carbon disulphide (?) are used; in the last-named case the yield from 100 kilos flowers is 10 grams oil.

Now trials have lately been made with varieties of the Japanese rose, *Rosa rugosa* Thunb., which have given extremely favourable results. Two varieties come above all under consideration, viz., *Rose de l'Hay* and *Roseraie de l'Hay*<sup>1)</sup>, which are so called from the township of l'Hay where the first trials were made to extract oil from these flowers. Like all Japanese roses, they have large blossoms, and are generally strongly built and very hardy. In Central France they blossom from the beginning of April to the beginning of November, and during all that time very abundantly. It is probable that at the Riviera they will blossom throughout the year. The cultivation must be arranged in such manner that the distances between the individual plants are 1 metre in every direction, so that (after deducting the roadways) the number of bushes is about 3200 to one acre. As one rose bush, from its third year, yields on an average 200 blossoms annually, each of which weighs about 4 grams, the result per bush is about 800 grams blossoms, and per acre about 2560 kilos blossoms, i. e. more than double the yield obtained with the rose cultivated at present.

<sup>1)</sup> According to the *Journal de la Parfumerie et Savonnerie françaises* [20 (1907), 146] the *Rose de l'Hay* has been obtained by J. Gravereaux, of l'Hay, by crossing *Rosa rugosa* with a cross between *Rosa damascena* and the species *Général-Jacqueminot*, whilst the *Roseraie de l'Hay* is a similar variety grown by Cochet-Cochet, of Coubert (department Seine-et-Marne).

According to the Vicomtesse de Savigny de Moncorps<sup>1)</sup>, who on her property at Seillans, department Var, has also made very satisfactory cultivation-experiments with the *Rose de l'Hay*, the blossoms have a most remarkable scent.

Experiments made at l'Hay show that an oil of exquisite quality can be obtained from the blossoms by extraction with low-boiling petroleum ether ( $d_{15^{\circ}}$  below 0,630). In this manner 8 grams oil were obtained from 10 kilos blossoms, (i. e. considerably more than the yield of the rose now cultivated), whilst on distillation with steam, 50 kilos blossoms only yielded 1 gram oil, although in the latter case of course rose water is also obtained. The quantity of oil obtained by extraction amounts to 2,05 kilos per acre, equal to a value of about 4000 francs, as compared with about 1500 francs value of the oil and water obtained by the distillation.

The *Revue de Grasse*<sup>2)</sup> quite justly emphasises that further experiments are necessary to ascertain whether the yields of blossoms and oil are really as high as those of the first experiments, and whether the rose oil obtained is of equally fine quality as that from the species of roses cultivated at present. Particularly from these points of view, it would be desirable to make a large number of cultivation-trials, so that it may be possible to form a perfectly clear opinion as to the value of the rose species of which the cultivation is to be taken up.

It may be interesting to mention here still that in the South of France cultivation-experiments are also made in other directions with the object to push the production of blossoms and of oil; for example, the "Nouveau Syndicat horticole de Magagnosc" has taken up the study of the question of replacing the species of violet now cultivated, by a variety which is more hardy, richer in blossoms, and if possible of a still more powerful scent than the present one.

From the same source we learn that the Chamber of Commerce of Digne has also recently occupied itself with the question whether the fact that in the department Basses-Alpes practically the same climatic conditions prevail as in Bulgaria, does not render the cultivation of oil roses in the valleys of the rivers Durance, Bléone, Asse and Verdon possible; and it has been decided to petition the Government to send an expert to carry on cultivation-experiments on a scientific basis. In the interest of the agricultural distress in the above-mentioned department, the cause of which must be more particularly looked for in the increasing depopulation, it can only be hoped that this step will lead to the desired result. As we ourselves

<sup>1)</sup> La Revue de Grasse 1907, No. 17.

<sup>2)</sup> Ibidem, No. 16.

through our Barrême works, stand in the closest relation to the districts in question, we will not fail to keep our readers informed on this subject.

**Rose Oil, German.** As could only be expected in face of the unfavourable weather conditions during the developing-period of the blossoms, this year's distillation result falls quantitatively far short of the average of previous years. Although the fields in flower afforded a magnificent spectacle, and the quantity harvested turned out normal, the roses were very poor in oil owing to the cool weather, — a fact which has also frequently been observed in Bulgaria in the course of the present season. In point of quality our rose oil can this year again be characterised as excellent, and we are convinced that our small stock will soon be cleared.

**Rose Oil, Russian.** For the production of rose oil and rose water, the inhabitants of the Eastern Trans-Caucasus<sup>1)</sup> have commenced the cultivation of a semi-double strongly smelling rose of Persian origin. In other districts, various plantations have been made of Kezanlik roses, particularly near Raevsk, Tremyuksk, Gelendshik, and New Athens. In the last-named place there exists also a factory of rose oil and rose water for which in Moscow 10 roubles per pood are paid; the oil costs about 115 roubles per lb. The first garden covering six dessiatines, which was laid out in 1898, is near New Pareula, where also a distillery is established which produces an excellent oil. This product is sold at 200 roubles per lb., the rose water at 10 roubles per pood. Smaller plantations of Kezanlik roses are also found in other districts of the Trans-Caucasus.

**Rosemary Oil.** On the part of the Dalmatian producers, a tendency is becoming apparent to raise the prices of the pure distillate; but the competition of the French product, which is offered this year again at very advantageous prices, has a counteracting effect on this tendency, and the manufacturers will doubtless be compelled, whether they like it or not, to abate their demands, if they do not wish to run the risk of having at least a portion of their production thrown on their hands.

**Sage Oil.** A Syrian oil of sage which we had received from Jaffa, whose mother-plant, according to Dr. A. Ginzberger, Assistant at the Botanical Institute of Vienna, is *Salvia triloba* L., had the following constants:  $d_{15}^{\circ}$  0,9116;  $n_D^{\circ}$  —  $3^{\circ} 28'$ ; ester no. 10,3, corresponding to 3,6% bornyl acetate; soluble in 15 to 16 and more vol. 70 per cent. alcohol; soluble in 1 and more vol. 80 per cent. alcohol. This oil differs from the Dalmatian oil of sage (from *Salvia officinalis* L.), which it resembles in the odour, especially by the low specific gravity and the optical lævorotation. It appears, however, to

<sup>1)</sup> Chemist and Druggist 70 (1907), 815.

be closely related to an oil from Palestine examined by us on a previous occasion<sup>1)</sup>, but unfortunately we were unable to ascertain from which species the previously examined sample had been distilled.

On the strength of our previous examination<sup>2)</sup> we had stated that in an oil of *Salvia officinalis* L., of Dalmatian origin, no camphor but only borneol was present. Now we recently availed ourselves of a further opportunity of examining a Dalmatian oil which had been supplied to us, the constants of which were as follows:  $d_{15^\circ}$  0,9282;  $\alpha_D + 10^\circ 2'$ ; acid no. 1,8; ester no. 12,6; ester no. after acetylation 52,1, corresponding to 14,8% borneol; soluble in 8 and more vol. 70 per cent. alcohol, soluble in 0,8 and more vol. 80 per cent. alcohol. On fractional distillation 72,6% of the oil passed over at 40 to 76° (6 mm. pressure); this consisted of pinene, cineol and thujone fractions; next followed a fraction from 76 to 92°, which represented 15,4% of the oil, and solidified on cooling; it contained, besides borneol, chiefly d-camphor, which was identified by the melting point of the oxime (118°). The distillation-residue amounted to 12%.

In consequence of this result, which took us quite by surprise, we also examined in this respect sage oils distilled by ourselves from the Dalmatian herb.

Normal oil:  $d_{15^\circ}$  0,9209;  $\alpha_D + 4^\circ 2'$ ; acid no. 1,4; ester no. 9,3; ester no. after acetylation 43,3, corresponding to 12,3% borneol; soluble in about 12 vol. 70 per cent. alcohol; soluble in 1 and more vol. 80 per cent. alcohol. On fractionating *in vacuo* (3 mm. pressure), 73,4% passed over from 40 to 65°; 7,5% from 65 to 80°, and 10% from 80 to 120°, whilst 9,1% remained behind in the residue. But in this case we were unable to separate camphor out of any of the fractions coming under consideration, not even by cooling in a freezing mixture.

Quite different, however, was the behaviour of the oil obtained by cohobation from the distillation waters; this contains the portions of the normal distillate which are readily soluble and suspended in water, and forms a part of the above normal oil. We call it

Water oil:  $d_{15^\circ}$  0,9503;  $\alpha_D + 10^\circ 25'$ ; soluble in 2,5 and more vol. 70 per cent. alcohol; soluble in 1,3 and more vol. 80 per cent. alcohol. In the distillation *in vacuo* (3 mm. pressure) there passed over 14,4% from 40 to 60°; 25% from 60 to 65°; 27,7% from 65 to 90°; 17,9% from 90 to 123°; residue 15%. From the fractions which passed over from 60 to 90°, borneol (m. p. 203°), and d-camphor (m. p. of the oxime 118°) could be separated off. The portions which passed over last on distilling the leaves, i. e. the

<sup>1)</sup> Report October 1905, 62.

<sup>2)</sup> Gildemeister and Hoffmann, The Volatile Oils, p. 614; Report October 1895, 42.

Oil of the last runnings, had the following properties:  $d_{15}^{\circ} 0.9524$ ;  $n_D + 7^{\circ} 30'$ ; not completely soluble in 10 vol. 70 per cent. alcohol; soluble in 2 and more vol. 80 per cent. alcohol. Of this oil there distilled from  $40$  to  $65^{\circ}$  (3 mm. pressure) 8.7%; from  $65$  to  $90^{\circ}$ , 8.5%; from  $90$  to  $115^{\circ}$ , 15.7%; from  $115$  to  $125^{\circ}$ , 37.9%; residue 29.2%. The portions which had passed over from  $40$  to  $115^{\circ}$  were once more fractionated, but we did not succeed in detecting in them either borneol or camphor.

These examinations confirm that both camphor and borneol are present in oil of sage. But it may possibly depend upon the manner of the distillation, whether the oil contains no camphor at all, or only very little camphor. To this must also be attributed that we were unable to detect camphor in the normal oil, although it is undoubtedly present in it.

**Sandalwood oil, East Indian.** The annual auction sales of sandalwood of the Mysore State will be held at the under-mentioned places on the dates specified against each: —

District	Koti		Tons
Shimoga	Tirthahalli	Nov. 18, 1907	188 $\frac{1}{2}$
	Sagar	" 21, "	178 $\frac{1}{2}$
	Shimoga	" 25, "	439 $\frac{1}{2}$
Kadur	Tarikere	" 28, "	146
	Chikmagalur	Dec. 2, "	182 $\frac{1}{2}$
Hassan	Hassan	" 5, "	128 $\frac{1}{2}$
Bangalore	Bangalore	" 9, "	71
Mysore	Seringapatam	" 12, "	257 $\frac{1}{2}$
	Hunsur	" 16, "	305
Total			1897

Particulars of the Fraserpett auction, to be held on Dec. 18, have not yet come to hand. — At the Tarikere auction there will be offered 125 tons sandalwood of season 1906/7.

It would be premature to draw already conclusions as to the probable course of the prices; as in last year, the behaviour of the native buyers, who at the last sales took up 1214 tons out of about 2934 tons, will decide the course of this year's market. If little inclination is shown here to buy, it may be assumed with a fair amount of certainty that lower prices will rule than at the last auctions. With regard to the spike disease, we have received no fresh reports.

Parry and Bennett<sup>1)</sup> report on the examination of two sandal oils which were probably adulterated with West Indian oil. The two samples were above all suspected on account of the low rotation ( $\alpha_D - 10^\circ$  and  $-9^\circ 30'$  respectively), and the low santalol content (82,2 and 83 % respectively), and on fractional distillation also gave results differing from those of normal oil, inasmuch as the corresponding fractions had very considerably lower rotations ( $\alpha_D - 4^\circ 30'$  to  $-14^\circ 45'$ , as compared with  $-14^\circ$  to  $-22^\circ$  in pure oil). The odour of the first fractions pointed to West Indian sandal oil. As the oils were soluble in 6 vol. 70 per cent. alcohol, Parry and Bennett believe that an oil had been used for the adulteration, from which the less soluble portions had been removed by fractional distillation.

Parry and Bennett conclude their work by suggestions with regard to the requirements which the next edition of the British Pharmacopœia should specify for sandal oil. They also recommend *inter alia*, that the first two tenths of the oil should be distilled off, and the fractions examined for their optical behaviour. According to this, a good sandal oil should answer the following requirements:  $d_{15^\circ}$  0,975 to 0,982;  $\alpha_D - 16^\circ$  to  $-20^\circ$ ;  $n_{D20^\circ}$  not below 1,503; santalyl acetate 4 to 6,5 %; total santalol at least 90 %; soluble in 5 vol. 70 per cent. alcohol;  $\alpha_D$  of the first 10 % and second 10 % of the distillate, not below  $-16^\circ$ .

Although pure East Indian oils may possibly also occasionally fail to answer these requirements, Parry and Bennett are quite correct in cautioning against a corresponding alteration in the limits of these values. We would add in this connection, that we consider 0,985 as upper limit of the specific gravity as more correct. It is, moreover, important to state the formula according to which the santalol content should be calculated; in view of recent examinations,  $C_{15}H_{24}O$  is the only formula which ought to come under consideration. The ester content fluctuates according to our experience between 2 and 6 %, calculated for  $CH_3COOC_{15}H_{23}$ .

For the principal constituents of East Indian sandalwood oil, viz.,  $\alpha$ - and  $\beta$ -santalol, Guerbet<sup>2)</sup> several years ago drew up the gross formula  $C_{15}H_{26}O$ . At that time<sup>3)</sup> we called already attention to the fact that, according to our own examinations made with santalol which had been regenerated from the phthalic acid compound, the formula  $C_{15}H_{26}O$  appeared doubtful, and should be replaced by one

<sup>1)</sup> Chemist and Druggist **71** (1907), 19.

<sup>2)</sup> Compt. rend. **130** (1900), 417 and 1324; Report April 1900, 42 and October 1900, 58.

<sup>3)</sup> Report April 1900, 43.

with a lower content of hydrogen. Shortly afterwards v. Soden<sup>1)</sup> also found for  $\alpha$ -santalol, which represents by far the larger portion of santalol, the formula  $C_{15}H_{24}O$ . This result is now confirmed by a new work by Semmler and Bode<sup>2)</sup> which for the rest deals with the question of the constitution of santalol.

According to this work, the authors were successful in converting santalol by oxidation with chromic acid in solution of glacial acetic acid, into the aldehyde santalal, which, regenerated from the semicarbazone (m. p. about  $230^{\circ}$ ) possesses the following properties: b. p.  $152$  to  $155^{\circ}$  (10 mm. pressure);  $d_{20} 0,995$ ;  $n_D +13$  to  $+14^{\circ}$ ;  $n_D 1,51066$ ; molecular refraction found 65,6, calculated for  $C_{15}H_{22}O/\overline{=}$  64,63. Crude santalal contained, besides admixtures of an alcoholic character, probably a lævorotatory santalal of the same formula  $C_{15}H_{22}O$ . As santalal could be converted into an oxime (m. p.  $104$  to  $105^{\circ}$ ), this into a nitrile, and the latter by saponification into an acid  $C_{15}H_{22}O_2$ , santalic acid (b. p.  $192$  to  $195^{\circ}$  at 9 mm. pressure), the aldehydic character of santalal is proved, which confirms the present assumption that santalol is a primary alcohol. The further oxidation of santalal with potassium permanganate or ozone, yielded the same tricyclo ecsantalic acid  $C_{11}H_{16}O_2$  as santalol itself (see below). By treatment with phosphorus pentachloride, a chloride was obtained from santalol, which on reduction with sodium and alcohol yielded a sesquiterpene  $C_{15}H_{24}$  ( $\gamma$ -santalene, b. p.  $118$  to  $120^{\circ}$  at 9 to 10 mm. pressure;  $d_{20} 0,9355$ ). When submitted to the action of sodium and alcohol, santalol did not change, but reduction with phosphorus and hydriodic acid in a sealed tube at  $180^{\circ}$  yielded a not entirely uniform hydrocarbon. Hydrocarbons were also formed when santalol was heated in a sealed tube to  $310^{\circ}$ .

The oxidation of santalol with potassium permanganate yielded in addition to dihydroxy-dihydro santalol  $C_{15}H_{26}O_3$ , tricyclo ecsantalic acid  $C_{11}H_{16}O_2$  (b. p.  $165$  to  $167^{\circ}$  at 10 mm. pressure; m. p. after crystallisation from water or glacial acetic acid  $71$  to  $72^{\circ}$ ), which supplied an insoluble copper and silver salt. From the methyl ester of this acid there was obtained by reduction with sodium and alcohol, the lævorotatory alcohol tricyclo ecsantalol  $C_{11}H_{18}O$  (b. p.  $130$  to  $132^{\circ}$  at 10 mm. pressure;  $d_{20} 0,9859$ ;  $n_D 1,49478$ ; molecular refraction found 49,1, calculated for  $C_{11}H_{18}O$  47,45, for  $C_{11}H_{18}O/\overline{=}$  49,66), which could be oxidised with chromic acid in solution of glacial acetic acid into the aldehyde tricyclo ecsantalal  $C_{11}H_{16}O$  (b. p.  $125$  to  $130^{\circ}$  at 13 mm. pressure;  $d_{20} 1,012$ ). When oxidising santalol with ozone, the same tricyclo ecsantalic acid was formed as in the oxidation

<sup>1)</sup> Arch. der Pharm. **238** (1900), 353; Report October 1900, 59.

<sup>2)</sup> Berl. Berichte **40** (1907), 1124.

with potassium permanganate. The acid is very stable against further oxidation with the above-mentioned substances, and other chemical actions, such as potash-fusion. For this reason it can no longer contain a double linking, but must possess a saturated tricyclic carbon system. It follows from the formation of the acid by oxidising away four carbon atoms of santalol, that the double-linking of this body must be situated in a side-chain. As the principal product of the oxidation of santalol with ozone, there was formed the above-mentioned tricyclo ecsantalol  $C_{11}H_{16}O$ , which after regeneration from the semicarbazone (m. p. about  $156^{\circ}$ ) had the following properties: b. p.  $112$  to  $114^{\circ}$  at 10 mm. pressure;  $d_{20} 1,01$ ;  $n_D 1,4076$ ;  $\alpha_D + 30^{\circ}30'$ ; oxime b. p.  $140$  to  $150^{\circ}$  at 10 mm. pressure;  $d_{20} 1,03$ ;  $n_D 1,506$ ;  $\alpha_D + 1^{\circ}$ .

On decomposing the ozonides of santalol by heating *in vacuo*, there was formed, owing to loss of  $CO_2$ , from the primarily formed tricyclo ecsantalic acid, the hydrocarbon  $C_{10}H_{16}$  (b. p.  $183,5$ ;  $d_{20} 0,885$ ;  $n_D 1,46856$ ;  $\alpha_D - 11^{\circ}$ ; molecular refraction found  $42,74$ ; calculated for  $C_{10}H_{16}$   $41,82$ , for  $C_{10}H_{16}/=43,52$ ), to which Semmler and Bode give the name nor-tricyclo ecsantalane, and which they regard as the mother-substance of all santalol derivatives described up to the present. The view of the authors, that in these bodies the presence of tricyclic saturated molecules must be assumed, is confirmed by the fact that it was possible to produce from them singly unsaturated bicyclic compounds.

The tricyclo ecsantalic acid could be converted by treatment with hydrogen chloride in methyl alcoholic solution, into a chlorinated ester, which on saponification with alcoholic potash yielded a bicyclo ecsantalic acid  $C_{11}H_{16}O_2$  (m. p.  $64^{\circ}$ ;  $[\alpha]_D - 41,81^{\circ}$  in alcoholic solution). This acid no doubt greatly resembles in its boiling and melting points the tricyclic acid, but it has a higher optical rotation, and is not, like the latter, very stable towards potassium permanganate and ozone; on the contrary, it is immediately oxidised further by these agents. It is consequently a bicyclic singly unsaturated acid. From its methyl ester was obtained by reduction with sodium and alcohol, bicyclo ecsantalol  $C_{11}H_{18}O$  (b. p.  $130$  to  $134^{\circ}$  at 9 mm. pressure;  $d_{20} 0,9791$ ;  $n_D 1,50051$ ;  $\alpha_D - 22^{\circ}$ ; molecular refraction found  $49,84$ , calculated for  $C_{11}H_{18}O/49,65$ ).

Tricyclo ecsantalol, when treated with phosphorus pentachloride, on reduction of the chloride thus formed with sodium and alcohol, was converted into bicyclo ecsantalane  $C_{11}H_{18}$  (b. p.  $72$  to  $74^{\circ}$ , at 10 mm. pressure;  $d_{20} 0,871$ ;  $n_D 1,4774$ ; molecular refraction found  $48,6$ , calculated for  $C_{11}H_{18}/48,1$ ).

The saturated nor-tricyclo ecsantalane  $C_{10}H_{16}$  could be converted by means of hydrochloric acid gas into the chloride  $C_{10}H_{17}Cl$ , and by treatment of the latter with alcoholic potash into the singly

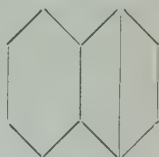
unsaturated, bicyclic hydrocarbon  $C_{10}H_{16}$ , nor-bicyclo ecsantalane (b. p.  $62$  to  $64^\circ$  at  $9$  mm. pressure;  $186$  to  $189^\circ$  at  $760$  mm. pressure;  $d_{20} 0,8827$ ;  $n_D 1,4779$ ; molecular refraction found  $43,59$ , calculated for  $C_{10}H_{16} \sqrt{43,52}$ ).

When heating santalol with alcoholic potash in a sealed tube to  $160^\circ$ , an alcohol  $C_{11}H_{18}O$  was formed ( $d_{20} 0,9738$ ;  $n_D 1,495$ ) which could be oxidised into the aldehyde  $C_{11}H_{16}O$ . The inversion of santalol by means of hydrochloric acid or glacial acetic acid and sulphuric acid, did not lead to uniform results, but Semmler and Bode believe from the rise in the refractive index of the strongly lævorotatory products obtained, to be justified in concluding that a disruption of the tricyclic santalol has taken place.

From the chlorinated methyl ester of tricyclo ecsantallic acid (see above) there was obtained by reduction with sodium and alcohol, dihydro bicyclo ecsantallic acid  $C_{11}H_{18}O_2$  (m. p.  $58^\circ$ ) and from the ester of this acid, in the same manner, dihydro bicyclo ecsantalol  $C_{11}H_{20}O$  (b. p.  $128$  to  $133^\circ$  at  $10$  mm. pressure;  $d_{20} 0,9724$ ;  $n_D 1,492$ ).

The determination of the molecular refraction of the tricyclic and bicyclic bodies described, resulted in so far in anomalies, that the calculated molecular refraction was exceeded by the one found. As in the bicyclic systems of tanacetone and sabinene also abnormal (i. e. too high) molecular refractions were found, to which Wallach<sup>1)</sup> in the case of the latter has particularly called attention, Semmler<sup>2)</sup> assumes that to such systems an increment is due, which is smaller than that of a double-bond (1,7), and should further be taken into account when calculating the molecular refraction. In the tricyclic systems this can be still larger than in the bicyclic.

With regard to the constitution of santalol and its derivatives, Semmler could not yet say anything definite, but he hopes to be able to decide by further experiments, whether a naphthalene ring with a bridge-bond, analogous to that of anthracene, belongs to them or whether they are based upon another system.



The first runnings of sandalwood oil had long ago been examined in detail by v. Soden and Müller<sup>3)</sup>, and also by Guerbet<sup>4)</sup>, and the presence in them of santene  $C_9H_{14}$ , a ketone  $C_{10}H_{16}O$ , sesquiterpenes  $C_{15}H_{24}$ , and also teresantallic acid  $C_{10}H_{14}O_2$  had been established. The last-named body has recently been the subject of an examination

<sup>1)</sup> Liebig's Annalen **347** (1906), 319; Berl. Berichte **40** (1907), 585; Report April 1907, 140.

<sup>2)</sup> Berl. Berichte **40** (1907), 1120.

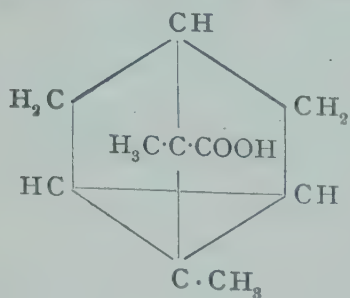
<sup>3)</sup> Pharm. Ztg. **44** (1899), 258; Arch. der Pharm. **238** (1900), 353 and 367; Report October 1900, 59.

<sup>4)</sup> Compt. rend. **130** (1900), 417 and 1324; Report April 1900, 42 and October 1900, 58.

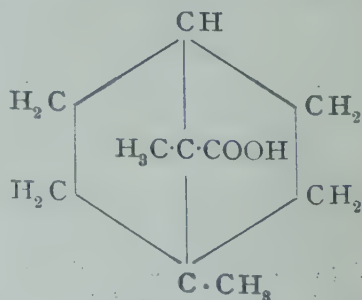
by Semmler and Bartelt<sup>1)</sup>, who found that although teresantalic acid does not stand in genetic relation to tricyclic  $\alpha$ -santalol, it also belongs to the tricyclic series. It melts at  $157^\circ$ , and has the specific rotatory power  $[\alpha]_D - 70^\circ 24'$  in 25 per cent. alcoholic solution. From its ester, which was formed from the white silver salt unaffected by light by means of methyl iodide (b. p.  $85$  to  $86^\circ$  at 11 mm. pressure;  $d_{20} 1,032$ ;  $n_D 1,47053$ ;  $\alpha_D - 63^\circ 45'$ ; molecular refraction found 48,8, calculated for  $C_{11}H_{16}O_2$  48,3), there originated on reduction with sodium and alcohol, the corresponding alcohol teresantalol  $C_{10}H_{16}O$  (m. p.  $113^\circ$ ;  $[\alpha]_D + 11^\circ 58'$  in alcoholic solution). The latter has an exceptional tendency for subliming, it possesses a camphor-like odour, and can be acetylated quantitatively. Its chloride, obtained by means of phosphorus pentachloride, yielded on reduction with sodium and alcohol the not quite pure hydrocarbon teresantalane  $C_{10}H_{16}$  (b. p.  $165$  to  $168^\circ$ ;  $d_{20} 0,892$ ;  $n_D 1,48033$ ).

When teresantalic acid was treated with hydrochloric acid gas in methyl alcoholic solution, it yielded a chloride (m. p.  $199^\circ$ ) which was converted by reduction with sodium and alcohol into dihydro teresantalic acid  $C_{10}H_{16}O_2$  (m. p.  $226^\circ$ ). By reducing the ester of this acid (b. p.  $88^\circ$  at 9 mm. pressure;  $d_{20} 1,0034$ ;  $\alpha_D - 13^\circ$  in 50 per cent. alcoholic solution;  $n_D 1,46757$ ; molecular refraction found 50,42, calculated for  $C_{11}H_{18}O_2$  50,23), Semmler and Bartelt obtained the corresponding alcohol dihydro teresantalol  $C_{10}H_{18}O$  (m. p.  $171^\circ$ ), which, however, is obtained more easily directly from teresantalol by treatment with hydrogen chloride, and subsequent reduction with sodium and alcohol.

With regard to the constitution of teresantalic acid and dihydroteresantalic acid, it is, in the opinion of the authors, established beyond doubt that the former is tricyclic saturated, and the latter bicyclic saturated. The action of hydrochloric acid would therefore split up a bridge-bond of the tricyclic system. Semmler and Bartelt imagine, owing to the similarity between the teresantalol series and camphor, that the constitution of the above-mentioned compounds is as follows:



Teresantalic acid



Dihydroteresantalic acid

<sup>1)</sup> Berl. Berichte 40 (1907), 3101.

The examination of the santalenes  $C_{15}H_{24}$ , also carried out by Semmler<sup>1)</sup>, showed a very close relationship of the two sesquiterpenes  $\alpha$ - and  $\beta$ -santalene to the two santalols  $C_{15}H_{24}O$ , as the former yielded the same derivatives by degradation as the latter. The two santalenes were separated by fractional distillation.

$\alpha$ -Santalene,  $C_{15}H_{24}$  (b. p.  $118$  to  $120^\circ$  at 9 mm. pressure;  $d_{20} 0,8984$ ;  $n_D 1,491$ ; molecular refraction found 65,8, calculated for  $C_{15}H_{24}/2$  66,15; calculated for  $C_{15}H_{24}/2$  64,45) yielded, on treatment with ozone in benzene solution in the presence of water, tricycloecsantalal  $C_{11}H_{16}O$  (see page 85), which shows that it is a tricyclic, singly unsaturated hydrocarbon.

$\beta$ -Santalene,  $C_{15}H_{24}$  (b. p.  $125$  to  $127^\circ$  at 9 mm. pressure;  $d_{20} 0,892$ ;  $n_D 1,4932$ ; molecular refraction found 66,55, calculated for  $C_{15}H_{24}/2$  66,15), when treated in the same manner as  $\alpha$ -santalene, yielded an aldehyde which could not yet be obtained pure of sesquiterpene, but which could be converted over the oxime and nitrile into bicycloecsantalic acid (m. p.  $62$  to  $64^\circ$ ). Semmler draws from this the conclusion of a bicyclic, doubly unsaturated molecule of  $\beta$ -santalene.

**Sassafras Oil.** Stimulated by the high prices of safrol, the trade in this article was brisk, with prices unchanged but firm.

**Savin Oil.** We recently succeeded in detecting citronellol in a fraction of oil of savin boiling higher than sabinol. We employed for this purpose a fraction boiling at  $78$  to  $94^\circ$  (4 mm. pressure), which at ordinary pressure boiled between  $220$  and  $237^\circ$ . The oil was heated on a water-bath with phthalic anhydride for 2 hours, and from the resulting acid phthalic ester the alcohol was liberated in the usual manner. The quantity of the alcohol purified by distillation with steam, which had a citronellol-like odour, was about 5 g. B. p.  $95$  to  $96,5^\circ$  at 6 mm. pressure,  $224$  to  $227^\circ$  at atmospheric pressure,  $d_{15} 0,8715$ . The silver salt of the citronellol phthalic ester acid formed from it melted after recrystallisation from benzene and methyl alcohol at  $126$  to  $127^\circ$ . Terpeneol could not be detected in a fraction boiling slightly lower.

In the further course of his studies of the oil of *Juniperus phoenicea* L., which, as is well known, is frequently mistaken for oil of savin, J. Rodié<sup>2)</sup> arrived at the following results, which we communicate here as a continuation of our previous information<sup>3)</sup>. Whilst the particulars hitherto given by Rodié dealt chiefly with the composition of the

<sup>1)</sup> Berl. Berichte 40 (1907), 3321.

<sup>2)</sup> Bull. Soc. Chim. IV. 1 (1907), 493.

<sup>3)</sup> Ibidem III. 35 (1906), 922; Report April 1907, 93.

terpene fraction of the oil (92.3 %), he now reports on the constituents of the fraction boiling above  $180^{\circ}$ , which represents 6.51 % of the oil. This fraction forms a brown-red viscid liquid with a peculiar odour reminding of juniper;  $d_{15^{\circ}}$  0.946;  $n_D^{20}$  1.010'; sap. no. 18.2, corresponding to 6.37 % ester  $\text{CH}_3\text{COOC}_{10}\text{H}_{17}$ ; sap. no. after acetylation 85.4, corresponding to 25.17 % alcohol  $\text{C}_{10}\text{H}_{18}\text{O}$ ; of these 5.03 % are combined and 20.14 % in the free state. With bisulphite solution Rodié isolated small quantities of an aldehyde which, however, he was unable to identify. This body, which represents about 0.0166 % of the oil of *J. phœnicea*, and which appears to be absent in the oil of other species of juniper, is, judging from the odour, probably a new aldehyde; its naphtho-cinchonic acid decomposes without melting at  $275$  to  $276^{\circ}$ ; the oxime is liquid; a semicarbazone could not be obtained; among the oxidation products obtained with potassium permanganate in alkaline solution, only carbonic acid could be detected. By further working up the aqueous solutions obtained on saponification of the fraction, Rodié established the presence of acetic acid. Of acids insoluble in water, which were purified by distillation *in vacuo* and rectified at ordinary pressure, caproic acid could be detected in the fraction of  $190$  to  $210^{\circ}$  at 732 mm.

**Spearmint Oil.** According to the reports from our New York branch, the stocks of this oil in the United States are very considerable, and as a good harvest is anticipated, lower prices may probably be expected. The quality of the article imported by us is unexcelled.

**Spike Oil.** The first offers of new distillate, which came to hand at the end of August, showed a considerable decline in the prices, and it is to be hoped that this article, which is of so much importance for the soap manufacture, will once more reach this year a normal price level, which will allow again of its use as a cheap perfume for soaps. The reports on the harvest from all producing districts are favourable.

**Star-Anise Oil.** Since we last reported on this article, the prices have been maintained, with slight fluctuations which are probably solely due to variations in the exchange, at an average level of 5/- cif. Hamburg. The highest point was reached in the middle of August with 5/3, whilst the cif. quotations have recently declined to 4/9. The tendency is weak, and we do not consider it impossible that we are again approaching the level of 1905, that is to say, prices of about 4/5 to 4/6. Generally speaking, this article is still greatly neglected. After a long interruption, a parcel of Tonquin star-anise oil, which is greatly in demand owing to its exquisite quality, was again offered about the beginning of September. But these small

supplies, unfortunately, are too unimportant to have any effect whatever on the market.

**Sumbul Oil.** A rather viscid sumbul oil distilled by ourselves, which had been produced in a yield of 1,37% from fresh slightly dried roots, possessed an olive green colour, and an odour reminding of angelica oil. Its constants were as follows:  $d_{15^{\circ}}$  0,9410;  $a_D + 6^{\circ}20'$ ; acid no. 7,0; ester no. 24,4; not completely soluble in 10 vol. 80 per cent. alcohol; soluble in every proportion in 90 per cent. alcohol.

**Oil of Thuja plicata.** W. C. Blasdale<sup>1)</sup> has obtained by distillation with steam from the air-dried leaves of *Thuja plicata*, a tree indigenous to the Pacific Coast of North America, which is universally known also under the name Red cedar or Canoe cedar, an essential oil with a terpene-like odour, of which he has determined the following constants:  $d_{15^{\circ}}$  0,8997;  $a_D + 1^{\circ}45'$ ;  $n_D$  1,4575; b. p. 150 to 225°. Apart from thujone, which was isolated and identified in the usual manner from a fraction of the b. p. 198 to 200° ( $d_{15^{\circ}}$  0,9142,  $a_D - 0^{\circ}52'$ ,  $n_D$  1,4532), no constituents could be further identified in the other portions of the oil. On distilling with steam the wood cut up into chips, Blasdale obtained, by extracting the distillate with ether, white crystals melting at 80°, which had the characteristic pungent odour of the wood, and to which the molecular formula  $C_{10}H_{12}O_2$  may possibly belong. The wood of *Thuja plicata*, a tree forming dense forests in Eastern Washington and Oregon, and resembling the white or swamp cedar of the Eastern districts, is worked up in enormous quantities into roof shingles.

**Thyme Oil.** J. Rodié<sup>2)</sup> has made experiments with Spanish thyme oils, in order to ascertain in how far from the specific gravity and solubility of these oils conclusions can be drawn as to their phenol-content. He has thereby arrived at the result that the phenol-content can only be judged approximately on the strength of the aforesaid physical properties, but that in a general way the following conditions apply: Of oils which possess a specific gravity above 0,950, and are soluble in 65 per cent. alcohol, it may be accepted that they contain more than 60% phenols. 40 to 60% may be contained in oils of a specific gravity of 0,922 to 0,950, if they are soluble in 70%, or better still in 65% alcohol. Oils with a specific gravity below 0,922, especially if they are insoluble in 70 per cent. alcohol, must be regarded as inferior owing to too small a content of phenols.

This method is only intended as an indication in cases where no phenol-determination can be carried out owing to want of time or material.

<sup>1)</sup> Journ. Amer. chem. Soc. 29 (1907), 539.

<sup>2)</sup> Bull. Soc. Chim. IV. 1 (1907), 236.

**Turpentine Oil.** In our Report<sup>1)</sup> we have already pointed out how important it is, in determining the iodine number of turpentine oil, to adhere strictly to the directions given, if comparable values are to be obtained. This is again confirmed by A. Mc Gill<sup>2)</sup>, who determined the iodine numbers of turpentine oil on the one hand with Hübl's iodine solution, and on the other with Hanuš's solution, varying the length of the reaction. Whilst the author, in using Hübl's solution, found iodine numbers which corresponded with Worstall's<sup>3)</sup> results, the iodine numbers obtained with Hanuš's solution were considerably lower. For this reason Mc Gill proposes to give preference to Hübl's method for determining the iodine number, and he mentions for pure turpentine oil, as lowest limits, the iodine no. 370 (if Hübl's solution is employed), or 200 (where Hanuš's solution is used). The commonly used adulterants lower the iodine number and also the refractive index, which latter Mc Gill particularly recommends for the purpose of judging turpentine oil. In the case of pure turpentine oils the index of refraction is about 1,47 at 20° C. According to the author it is easy to distinguish pure turpentine oil from adulterated, if from 100 cc. oil 25 cc. are distilled off while the boiling temperature is watched, and if the iodine number and refractive index of the distillate are also determined.

A. Tschirch<sup>4)</sup> has jointly with H. Schulz submitted the turpentine of *Pinus halepensis*, which is very largely used on the continent of Greece for the production of the so-called resinate wine, to a thorough investigation.

As Professor Dambergis, of Athens, informed the authors, the turpentine is produced in nearly all provinces of Greece. It is usual either to make deep incisions in the trunks (according to the Austrian method) through which the resin quickly flows away, or in the French manner to cut rather shallow notches and place a wooden receptacle below these, in which the balsam is collected. The crude resin is employed in the manufacture of resinate wine; the waste products after emptying the wine barrels, are worked up into turpentine oil and colophony. Now as the turpentine production has increased largely in recent times, also the crude turpentine is partly worked up directly into oil and colophony. *Pinus halepensis* is the only tree in Greece which is used for the production of turpentine. The solubility of the balsam in wine is naturally very slight ( $1\frac{1}{2}$  to  $1\frac{1}{2}$  in 10000) but this quantity is quite sufficient to impart to the wine the peculiar

<sup>1)</sup> Report October 1904, 85.

<sup>2)</sup> Journ. Soc. chem. Industry 26 (1907), 847.

<sup>3)</sup> Ibidem 23 (1904), 302. Report October 1904, 85.

<sup>4)</sup> Arch. der Pharm. 245 (1907), 156.

taste and the characteristic aroma. The essential oil which was isolated in the course of the examination, and which was obtained in a yield of 21%, had  $d_{20} 0.8971$ , and the boiling point  $150$  to  $152^{\circ}$ ; when exposed to the air it became dark, and resinified gradually. On fractional distillation, clear limpid first runnings boiling between  $120$  and  $150^{\circ}$  were obtained; the bulk, of a pleasant odour and somewhat dark, passed over between  $151$  to  $155^{\circ}$ ; a small quantity of brown last runnings boiled from  $155$  to  $190^{\circ}$ .

The high prices of American turpentine oil have directed attention to cheaper kinds of oil of turpentine. To the latter belongs the Finnish pine tar oil, the price of which is about half that of the American oil. But as its pungent odour and also its yellow colour render its use for the brighter paints objectionable, O. Aschan<sup>1)</sup> has attempted to determine the impurities which are the cause of these faults, and to find means by which they may be removed. Finnish pine tar oil is obtained as a by-product in the preparation of wood-tar from conifers. It is separated from the tar-water on which it floats, and once more distilled with the addition of lime. The crude material for the tar-distillation consists of the stumps of the felled pines and firs, which are available in large quantities in the interior of Finland.

Aschan examined an oil with a pungent odour, which passed over first when the crude turpentine oil was distilled with steam. On fractional distillation it boiled between  $28$  and  $160^{\circ}$ . The portions boiling below  $40^{\circ}$  had an aldehyde-like odour, which from  $65^{\circ}$  upwards became suffocating like quinone. From this point the colour of all the fractions was green-yellow to orange-yellow, and this colour could not be removed even by repeated distillation. A more detailed examination showed that diacetyl and its homologues produce both the pungent odour and the coloration. All fractions were unsaturated, and gave an aldehyde reaction. In the fractions boiling below  $40^{\circ}$ , furane was detected, and in those boiling between  $60$  and  $70^{\circ}$ ,  $\alpha$ -methyl furane, the latter in large quantity. In the fractions of the boiling point  $90$  to  $100^{\circ}$ , methyl isobutyrate was present. Benzene and its homologues were also detected.

For the purification of Finnish pine tar oil the following come under consideration: 1. dilute caustic soda lye, which condenses diacetyl and its homologues to quinones of the benzene series, and thus easily removes them, and which also destroys the offensive impurities of which small quantities are present in the first runnings. 2. Sulphuric acid, which in moderate concentration resinifies furane, the aldehydes,

<sup>1)</sup> Farmaceutisk Notisblad 1907, 93; accord. to Apoth. Ztg. 22 (1907), 483.

and the unsaturated compounds. The terpenes, however, are also attacked by strong sulphuric acid.

Whether Finnish pine tar oil, which according to Aschan's examinations contains only 6,14% pinene, and for the rest consists of sylvestrene, l-limonene and dipentene, can also be employed for therapeutic purposes, is a question which still remains to be solved.

Before the New England Section of the Society of Chemical Industry<sup>1)</sup>, Teeple read a paper on the production of turpentine oil from waste wood. Starting from the well-known method of production of turpentine resin, Teeple stated that in the last few years the "cup and gutter" system of tapping had been adopted more and more,<sup>2)</sup> as this does not make such a heavy demand on the trees as the old "boxing" system. Owing to the fact that the tree is constantly wounded afresh, the wood in the last-named method is in the neighbourhood of the wound in time entirely blocked up by rosin ducts, the content of which differs from the exuding resin only by a somewhat lower oil-content. If the tree breaks from any cause whatever — either by winds, or by loss of vitality, — the wood saturated with rosin (so-called "light wood") remains standing up to the height of the tappings, say about 10 to 15 feet; the content of rosin protects this "light wood" from rotting which rapidly attacks the sap wood. As long ago as 1841 it was started to make use of this "light wood" — which for the rest is very heavy, and probably owes its name to the fact of its being used for torches — by submitting it to dry distillation. An equally rich yield of wood spirit, acetic acid, charcoal, gas, and tar was hoped for, as from "hard wood", but experience showed that a great mistake had been made in calculating the yield of these products, and partly also in their utilisation. Various modifications of the retorts, and alterations of the apparatus and the working methods, did not lead to the desired end, so long as the process was based upon the principle of dry distillation. More successful were the trials, first made as long ago as 1865, and recently repeated, to heat the wood in rosin-baths, and blow in steam; but this method had the disadvantage of heavy expense and risk of fire, whilst the yields also fell short of the expectations. Next Hull's process (1864) was tried, in which the ground wood was distilled in vertical retorts heated from beneath with superheated steam. This process has in practice the disadvantage that the hot steam at once chars a portion of the wood, and consequently effects partial dry distillation, the products of which pass over as impurities of the turpentine along with the latter; moreover, not sufficient

<sup>1)</sup> Journ. Soc. chem. Industry **26** (1907), 811.

<sup>2)</sup> Comp. Report April 1906, 65.

care was exercised to secure uniform superheating. Teeple expects the best result from the use of non-superheated steam, a method first patented to Leffler in 1864, then forgotten, and lately again rejuvenated by Krug. In this case the wood material is first distilled exhaustively with steam, and the wood then worked up further by dry distillation or otherwise. The turpentine oil is consequently not heated to such a degree that it distils out of the retort, — i. e., superheating does not take place here. In plants in which this principle is adopted, great value is attached to the mechanical side of the work, for example the filling and emptying of the retorts, the correct distribution of the steam, the agitation of the wood inside the retorts, etc. The author, who is apparently fully acquainted with all the different methods coming under consideration, as well as with their execution, states the yields in this process to be 6 to 25 gallons of oil per cord<sup>1)</sup> of wood, or on the average 12 to 15 gallons. There exist in the United States all in all about 80 installations for working up "light wood" and waste wood from the saw mills. If the work is carried out properly, the turpentine oil produced by these processes is said to be at least equal to that obtained from turpentine resin — and possibly superior, owing to its uniform character. With regard to the wood from which the oil has been distilled out, and which has in no way been altered in its structure by the distilling process, its utilisation is still an unsolved question. A portion of it is used as fuel; attempts to destructively distil the rest failed, unless retorts were used in which the wood could be agitated on account of the bad conductivity. Some success has attended the efforts to work up the wood which had been distilled out with steam, into inferior kinds of paper, or to isolate the colophony; but up to the present this has not gone beyond the experimental stage. So much is certain that it is not possible to use the same retort for steam distillation as well as for destructive distillation.

We read in a Report<sup>2)</sup> from the German Agricultural Expert in the United States, that in view of the constant clearing of the pine forests there, a substitute for the trees is looked for, and that this has been found to some extent in the stumps of the pines. Successful attempts have been made to work up these stumps into oil by distillation with steam, and a company has been formed at Hinckley, in North Minnesota, which obtains from the farmers against compensation the right to remove the stumps in the denuded forests areas from the ground for the purpose of oil pro-

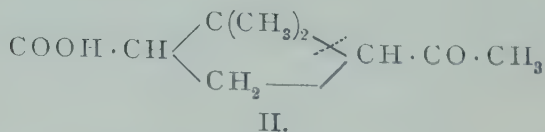
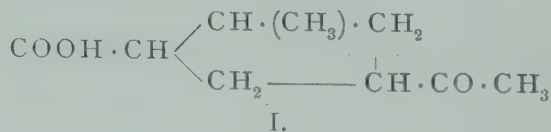
<sup>1)</sup> 1 cord = 8 × 4 × 4 feet.

<sup>2)</sup> Nachrichten für Handel und Industrie 1907, no. 33.

duction. If the future proves that these results are crowned with success, a new and important source of supply for the production of a "turpentine oil" might thus be opened up, and at the same time colonisation be facilitated.

According to a method indicated by Lorenz<sup>1)</sup> but not described more in detail, it is possible to "extract" from pine wood "turpentine" and rosin by means of distillation *in vacuo*, at a temperature at which the wood is not decomposed. Both products are said to be of best quality, and the turpentine especially "water white".

**Oil of Umbellularia californica.** We have already on a previous occasion referred to F. Tutin's<sup>2)</sup> experiments for clearing up the constitution of umbellulone. The continuation of this work deals in the first place with the reduction of umbellulonic acid<sup>3)</sup>. If this acid is treated with sodium and alcohol, there is formed, with ring-disruption and addition of two atoms hydrogen, a hydroxy acid with a side-chain. This acid yields a lactone of the b. p. 246 to 248°, and is oxidised by permanganate in the presence of an excess of alkali, into acetic acid and isopropyl succinic acid. As has been shown at the time, umbellulonic acid must contain either a methyl pentamethylene, or a dimethyl tetramethylene ring. A hydroxy acid which on subsequent oxidation yields acetic acid and isopropyl succinic acid, can only originate from the ketonic acids:—



and would correspond to the formula

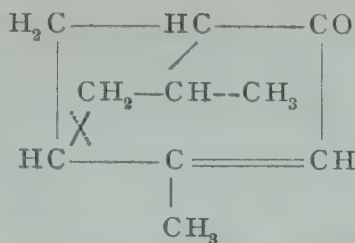


i. e. it would be a  $\delta$ -hydroxy- $\alpha$ -isopropyl caproic acid. Now, as has previously been proved, formula II belongs to pinononic acid. For this reason, only formula I can apply to umbellulonic acid, and further, for umbellulone itself the formula previously drawn up:—

<sup>1)</sup> Oil, Paint and Drug Reporter **69** (1906), 38. Accord. to Zeitschr. f. angew. Chem. **20** (1907), 626.

<sup>2)</sup> Journ. chem. Soc. **89** (1906), 1104; Report October 1906, 79.

<sup>3)</sup> Ibidem **91** (1907), 271.



If hydroxylamine-dihydroumbellulone oxime, whose production has already previously been mentioned<sup>1)</sup>, is reduced with sodium and alcohol, there is formed (as was proved by Tutin<sup>2)</sup>), probably with ring-disruption at the same place at which umbellulonic acid is split up on reduction, a base boiling at 136 to 138° (50 mm. pressure), and dissolving in water with evolution of heat, which judging from its derivatives (dibenzoate [m. p. 212 to 213°], dihydrochloride [not yet melting at 305°, but gradually becoming decomposed], dibenzoyl compound [m. p. 194°]), represents aminotetrahydro umbellulyl amine, to which belongs either the formula C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>, or, more probably, C<sub>10</sub>H<sub>22</sub>N<sub>2</sub>.

**Wintergreen Oil.** For the reasons mentioned in our last Report, this article has again enjoyed a very brisk demand, especially in the United States, which has driven the prices continuously upwards. The supplies came in only very slowly, so that business was extremely lively, and the quotations finally advanced to \$ 3.75 for the oil from *Gaultheria procumbens* (from the leaves) and \$ 2.25 for the distillate of *Betula lenta* (from sweet birch). The first-named oil, as is well known, is consumed almost exclusively in America, whilst the kind exported consists only of the last-named quality, that is to say does not originate from *Gaultheria procumbens*, but from *Betula lenta*. We mention this, as there is a good deal of confusion on this point.

Dodge<sup>3)</sup> read a paper before the New York Section of the American Chemical Society on the subject of natural and artificial methyl ester of salicylic acid. The ester occurring naturally, wintergreen or gaultheria oil, contains 2 to 5% of other substances which have a very important bearing on the odour. The constants found in literature on the specific gravity of the synthetic ester, vary considerably, and are mostly incorrect. Dodge purified the ester by freezing at — 5°; the crystals melting at — 1.5° were white, well-formed, and resembled those of thymol. The specific gravity of the frozen-out ester was 1.1899. The analysis of the natural and artificial esters is well known and simple; but it is important to ascertain a

<sup>1)</sup> Ibidem 85 (1904), 639; Report October 1904, 87.

<sup>2)</sup> Ibidem 91 (1907), 275.

<sup>3)</sup> Chem. Ztg. 31 (1907) 642.

possible adulteration of the natural product with synthetic ester. Dodge was able to determine that the latter always contains phenol, although the quantity of the latter is often very minute.

**Wormwood Oil.** As already mentioned by us in our last Report<sup>1)</sup>, the French Government has started a very energetic campaign against the consumption of absinthe. Sanglé-Ferrière and Cuniasse<sup>2)</sup> have also entered the arena, and oppose the frequently expressed wrong opinion that the injurious character of this liqueur can be judged from the occurrence of a more or less severe turbidity when a definite quantity of water is added.

The authors examined the essential oils used in the manufacture of absinthe for their behaviour towards water. Each of the oils was dissolved in 70 per cent. alcohol in the proportion of 3 g. per litre, and to this solution  $\frac{2}{3}$  of its volume distilled water was added. The turbidity numbers determined with the help of a diaphanometer, were for the individual oils as follows: wormwood oil 40,4; oil of tansy 53,0; hyssop oil 34,0; coriander oil 34,0; fennel oil 12,0; star anise oil 3,4; anise oil 2,2. The numbers indicate the height in millimetres at which the finest lines of the diaphanometer screen can no longer be distinguished. From these results it is quite clear that the occurrence of turbidity when water is added, not only can be no criterion for the injurious character of the oil in question, but on the contrary, in the conclusions drawn from it up to the present, directly reverses the actual conditions. The strongest turbidity was caused by the comparatively harmless and non-poisonous spice oils, e. g., anise oil, star-anise oil, and fennel oil, which on the strength of the turbidity method should be taken as the most injurious ones; in the case of the most strongly toxic thujone-containing oils, wormwood oil and oil of tansy, whose total quantity represented only  $\frac{1}{5}$  to  $\frac{1}{6}$  of the oil-content of absinthe, the turbidity was the most feeble. In the place of this purely arbitrary "method" which misrepresents the actual facts, the authors propose that the total oil-content of the liqueur be determined and a test be made for the presence of thujone.

With regard to the cultivation of the plants employed for the production of absinthe, Roure-Bertrand Fils<sup>3)</sup> give some information, with suitable illustrations, for which J. Boyer has supplied the material. The following plants come under consideration for the absinthe industry: the common wormwood (*Artemisia Absinthium*), small-sized wormwood (*Artemisia pontica*), hyssop (*Hyssopus officinalis*), and balm (*Melissa officinalis*). Whilst common wormwood serves to

<sup>1)</sup> Report April 1907, 103.

<sup>2)</sup> Journ. de Pharm. et Chim. VI. 25 (1907), 428.

<sup>3)</sup> Bericht Roure-Bertrand Fils, April 1907, 43.

give to the liqueur the characteristic spicy and bitter taste, the other herbs help to form the aroma and the pleasant taste.

Common wormwood is gathered by cutting the shrubs close to the ground with a pair of hedge shears; the cut-off plants are spread out on frames to dry. When the wormwood is dry it is cut in the same way as chaff and packed in bags which, when filled, weigh 80 to 90 kilos.

*Artemisia pontica* is usually cut with a scythe, gathered on linen sheets of 1 square metre, and finally tied into a bale. What has been cut off during the day is brought into the store every evening, as this plant must not be left in the open air over night.

The cultivation of hyssop and balm is carried on in the same manner. The young plants are partly grown from seed, and partly obtained from old shrubs which are divided into several parts; the use of cuttings is also common. For gathering the plants a kind of sickle is employed; they are dried on a frame work similar to that used for common wormwood.

**Wormseed Oil, American.** Owing to Brüning's publications to which we referred in our last Reports, the demand for this anthelmintic was very brisk, and occasionally it was not possible to meet the requirements to their full extent. The stocks in the United States have dwindled down very much, and it is yet too early to draw conclusions as to the results of the new harvest which commences in the course of this month.

On several occasions<sup>1)</sup> we have already discussed the activity of American or Baltimore wormseed oil as an anti-ascaridiac. Further experiments made by H. Brüning<sup>2)</sup> on children have confirmed that *Oleum Chenopodii anthelmintici* does not only deserve to rank side by side with santonin as its equal, but that disturbances which have always to be taken into account when the last-named remedy is administered, never occur in a manner worth mentioning if wormseed oil is taken as an anthelmintic. This also applies to the active principle  $C_{10}H_{16}O_2$  discovered by us in the oil. Although this body naturally proved more active than the oil itself in the pharmacological experiments made with it, it was a remarkable fact that in patients suffering from worms no noteworthy difference could be observed with regard to its action as compared with that of the oil.

The children affected received every morning three times 8 to 15 drops, according to their age (measured with a dropping glass, 0,5 to 1,0 g. pure oil) stirred up in sugar water, and subsequently a laxative in the form of castor oil, *Pulv. Curellae*, or such like, at

<sup>1)</sup> Report October 1906, 81; April 1907, 102.

<sup>2)</sup> Deutsche Mediz. Wochenschrift 1907, No. 11 (reprint).

intervals of 1 hour. If no action took place by late in the afternoon, the laxative was given once more. In this manner it was possible to drive off the ascarides in almost every case by one single cure, and only in a few cases was a repetition found necessary. The administration of a suitable laxative is required for this reason, that the experimental researches have shown that the ascarides are not destroyed by wormseed oil, but are only narcotised, and also because the too prolonged presence of the oil in the body would cause irritation of the mucous membrane of the intestine, and give rise to admixtures of mucus to the stools. The children take the preparation in the above-mentioned form in almost every case without repugnance, but in order to cover the peculiar odour and taste of the oil, it is advisable to follow up the dose with a little hot milk.

On the strength of his numerous experiments with wormseed oil Brünig emphasises again that the favourable results call unquestionably for further trials, and that to all appearances the oil deserves to be included in the German Pharmacopœia, the more so, as it is official as an antiascaridiac in America.

From a copy kindly forwarded to us, we learn that F. Thelen<sup>1)</sup> has obtained equally favourable results with children. He reports on 32 further cases in which both the oil and the body  $C_{10}H_{16}O_2$  left nothing to be desired with regard to the reliability of their action. The author regards the oil as a specific against ascaridiasis.

**Ylang Ylang Oil "Sartorius".** Business in this speciality of ours was very brisk, and we are pleased to be able to state that the excellent quality of our brand has been the means of introducing it to almost all the principal firms among the consumers. As there is occasionally a scarcity in this oil, we would point out that it is advisable to secure the necessary supplies by contract. We find practically no demand for the ordinary commercial qualities, as we possess in our artificial ylang ylang oil (German Patent no. 142859) a substitute which is preferred by every expert to the average qualities.

According to official statistics, the value of the ylang ylang oil exported in 1906 from the Philippines was

99009 dollars

against 93918 „ in 1905.

Three-fourths of the total export was shipped to France, but it is impossible to draw from this a correct conclusion as to the consumption of the oil in that country, as all our supplies, for example, usually come via Marseille.

<sup>1)</sup> F. Thelen, *Klinische Erfahrungen über das amerikanische Wurmsamenöl als Antiascaridiacum bei Kindern.* (Clinical experiences with American wormseed oil as an antiascaridiac in children.) Thesis, Rostock, 1907.

## New essential oils.

**Magnolia Oil.** From Japan we received a sample designated as magnolia oil, as to the origin of which we were unable to ascertain any further details. It was a limpid, bright-yellow oil, and had the following constants:  $d_{15}^{\circ}$  0,9100;  $\alpha_D + 14^{\circ} 10'$ ; soluble in about 7 and more vol. 80 per cent. alcohol with minute turbidity. Of constituents, cineol and phellandrene could be detected; the oil probably contains also linalool and terpineol. According to the results of this examination, it appears to be out of the question that this magnolia oil is identical with the kobushi oil from *Magnolia Kobus* D. C.<sup>1)</sup> previously examined by us.

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## Pharmacopœias.

### American Pharmacopœia (U. S. Ph.).

On the part of the American Pharmacopœia Committee, Supplements to the U. S. Ph. have been published on the 1 May and 1 June 1907, which contain partly corrections of various statements, and partly additions to the individual articles. In the case of the essential oils, various alterations have also been made, but unfortunately not to such an extent as in our opinion appeared desirable. We quote the various data below without comment, as all further particulars are found in our previous discussion of the Pharmacopœia<sup>2)</sup> to which we here beg to refer.

**Anise Oil.**  $d_{25}^{\circ}$  0,975 to 0,988;  $\alpha_{D25}^{\circ}$  to  $-2^{\circ}$ .

**Caraway Oil.**  $d_{25}^{\circ}$  0,900 to 0,910.

**Copaiba Oil.** The requirement of solubility has been cancelled.

**Erigeron Oil**<sup>1)</sup>.  $\alpha_{D25}^{\circ}$  not below  $+45^{\circ}$ .

<sup>1)</sup> It should be mentioned here still that in recent times we have had to deal repeatedly with authentic erigeron oils which had a distinctly higher specific gravity than that allowed by the American Pharmacopœia. The specific gravities of the oils in question amounted up to 0,887 at  $\frac{15^{\circ}}{15^{\circ}}$ , corresponding to 0,881 at  $\frac{25^{\circ}}{25^{\circ}}$ .

**Eucalyptol.**  $d_{25}^{\circ}$  0,921 to 0,923.

**Eugenol.**  $d_{25}^{\circ}$  1,066 to 1,068.

**Oil of Juniper berries.** The requirement of solubility is left out.

**Lavender Oil.**  $d_{25}^{\circ}$  0,875 to 0,910.

<sup>1)</sup> Report October 1903, 78.

<sup>2)</sup> Comp. Report April 1906, 69.

**Lemon Oil.**  $a_{D25^{\circ}}$  not below  $+58^{\circ}$ .

**Nutmeg Oil.**  $d_{25^{\circ}}$  0,884 to 0,924. The requirement of rotation has been left out.

**Peppermint Oil.**  $a_{D25^{\circ}}$   $-20^{\circ}$  to  $-33^{\circ}$ ; ester-content (menthyl acetate) at least 6%.  
 †

**Pimenta Oil.**  $d_{25^{\circ}}$  1,028 to 1,048.

**Rosemary Oil.** Ester-content (bornyl acetate) at least 2,5%; total borneol at least 10%.

**Safrol.**  $d_{25^{\circ}}$  1,098 to 1,100.

**Sandalwood Oil.**  $d_{25^{\circ}}$  0,965 to 0,980.

**Sassafras Oil.** Special requirements of solubility exist no longer.

**Thyme Oil.** Colourless or reddish.

**Wormseed Oil, American.** Requirements of specific gravity, rotation, and solubility have been cancelled.

## Danish Pharmacopœia.

(Pharmacopœa danica 1907).

A new edition of the Danish pharmacopœia has now also made its appearance, a fact which induces us to discuss here the articles dealing with essential oils in a like manner as in the case of the other pharmacopœias of which up to now new editions have been published.

As compared with the old Pharm. dan. 1893, no additional directions for testing have been given, so that generally only the colour, odour, specific gravity, and solubility are taken into consideration. On the other hand, a whole number of erroneous statements in the old Pharmacopœia have been corrected, and the requirements specified by the new edition may be characterised almost without exception as being to the point.

No oil has been newly added, but several oils hitherto official are now no longer included, for example bergamot oil, cajeput oil, cassia oil, oil of juniper berries, mace oil, oil of sweet marjoram, mustard oil, and crude oil of turpentine.

The alcohols which come under consideration for testing the oils, are alcohol (Vinaand, Spiritus concentratus) with 90 to 91 per cent. by volume, and dilute alcohol (Fortyndet Vinaand, Spiritus dilutus) with 68 to 70 per cent. by volume.

The individual oils may now follow:—

**Anise Oil.** (*Aetheroleum anisi*). At low temperatures, a white crystalline mass, which commences to melt at  $15^{\circ}$ , and at about  $20^{\circ}$

represents a colourless or faintly yellowish, strongly refractive liquid;  $d_{15^\circ}$  0,980 to 0,990<sup>1)</sup>; soluble in 1,5 to 5 vol. alcohol.

<sup>1)</sup> It is recommended to determine the specific gravity at 20°, as anise oil sometimes solidifies already spontaneously at 15°; the above limits of value also apply to 20°.

**Clove Oil** (*Aetheroleum caryophylli*). In the fresh state bright yellow, in the course of time acquiring a brownish colour;  $d_{15^\circ}$  1,045 to 1,070; soluble in 2 vol. dilute alcohol.

**Fennel Oil** (*Aetheroleum foeniculi*). Colourless or faintly yellow;  $d_{15^\circ}$  0,965 to 0,975; soluble in an equal vol. alcohol; when cooled to about + 5°, it should solidify to a crystalline mass.<sup>1)</sup>

<sup>1)</sup> Solidification must sometimes be started by inoculation with a small quantity of solid anethol, as under certain conditions fennel oil may be cooled much below its solidification point without actually solidifying.

**Lavender Oil** (*Aetheroleum lavandulae*). Light yellow or greenish yellow;  $d_{15^\circ}$  0,885 to 0,895; soluble in every proportion in alcohol, and in 3 vol. dilute alcohol.

**Lemon Oil** (*Aetheroleum citri*). Light yellow;  $d_{15^\circ}$  0,858 to 0,861<sup>1)</sup>; with 5 vol. alcohol it forms a not quite clear solution; lemon oil must not show a strong acid reaction.

<sup>1)</sup> It would have been better to have given 0,857 as lower limit of value.

**Menthol** (*Mentholum*). Colourless, brittle, needle-shaped crystals, not moist. M. p. 43°<sup>1)</sup>; b. p. 212°<sup>2)</sup>; only very slightly soluble in water; very readily soluble in alcohol, ether, chloroform, and fatty oils. When heated in an open dish on a water-bath, menthol should evaporate completely.

<sup>1)</sup> The m. p. of menthol, taken exactly, lies between 43,5 and 44,5°.

<sup>2)</sup> Menthol boils about 217° if the mercury thread of the thermometer is entirely placed in the steam.

**Oil of Parsley Seed** (*Aetheroleum petroselini*). Viscid, yellowish to brownish yellow;  $d_{15^\circ}$  1,050 to 1,100; soluble in an equal vol. alcohol.

**Peppermint Oil** (*Aetheroleum menthae piperitae*). Colourless, yellowish or greenish yellow;  $d_{15^\circ}$  0,900 to 0,920<sup>1)</sup>; at 20° soluble in 3 to 5 vol. dilute alcohol; when more solvent is added, at most a slight cloudiness may occur.

<sup>1)</sup> According to the specific gravity, both English and American oils are allowed.

**Rose Oil** (*Aetheroleum rosae*). Light yellow, sometimes greenish yellow and fairly viscid. At a temperature below 18 to 21°, pointed or laminated crystals separate out from the oil, and if cooled further, the oil solidifies completely;  $d_{20^\circ}$  0,855 to 0,870; only partly soluble in alcohol.

**Rosemary Oil** (*Aetheroleum rosmarini*). Colourless, or yellowish to greenish yellow;  $d_{15}^{\circ}$  0,900 to 0,920; soluble in 0,5 and more vol. alcohol.

**Sandal Oil, East Indian** (*Aetheroleum santali*). Fairly viscid; light yellow to yellow;  $d_{15}^{\circ}$  0,975 to 0,980<sup>1</sup>); at 20° soluble in 5 vol. dilute alcohol, the solution must also remain clear if more alcohol is added.

<sup>1</sup>) The upper limit of value of the specific gravity is given too low; it should be 0,985.

**Thyme Oil** (*Aetheroleum thymi*). Colourless or yellowish, subsequently red-yellow;  $d_{15}^{\circ}$  0,900 to 0,930; soluble in half its vol. alcohol.

**Thymol** (*Thymolum*). Colourless, transparent crystals; m. p. 51 to 52°<sup>1</sup>); b. p. 228 to 230°<sup>2</sup>); completely volatile at the temperature of the water-bath. Molten thymol floats on water, crystallised thymol sinks in it. Soluble in 1100 vol. water, very readily in alcohol, ether, and chloroform, also in 2 vol. caustic soda liquor (containing 10% NaOH). Identity reactions and test for carbolic acid.

<sup>1</sup>) The melting point lies between 50,5 and 51,5°.

<sup>2</sup>) Thymol boils between 233 and 234°, if the mercury thread of the thermometer is placed entirely in the steam.

**Turpentine Oil, purified** (*Aetheroleum terebinthinae*). Colourless;  $d_{15}^{\circ}$  0,860 to 0,870; soluble in about 10 vol. alcohol. If the oil is shaken with an equal vol. water, the latter must not take an acid reaction; 10 cc. oil when evaporated on a water-bath may leave behind only a trace of solid residue.

## Japanese Pharmacopoeia.

With regard to the extension of the time during which the preparations imported from abroad are still tested according to the old Pharm. Japon. II., we have reported in detail on p. 9.

## Chemical preparations and drugs.

**Civet.** The price lately paid for the pure original quality is about 10% higher than formerly, and the article supplied frequently left much to be desired in point of quality. It is well known that we have always a considerable stock at our disposal of selected original horns, and we are still in a position to supply this to our friends at the prices quoted up to the present, provided not too great a call is made upon our stock by an exceptionally heavy demand in the near future.

**Copaiba balsam.** In *The Chemist and Druggist*<sup>1)</sup> attention is called to the adulterations of copaiba balsam which occur frequently, owing to the high prices. Whilst gurjun balsam is no longer used as an adulterant because it is too readily detected, it appears that in recent times the African copaiba balsam is used more and more for that purpose. At any rate, it is a remarkable fact that copaiba balsam oil, for which the British Pharmacopœia has fixed  $\alpha_D - 14^\circ$  to  $- 17^\circ 30'$  as limits of value (we fixed  $- 7^\circ$  to  $- 35^\circ$ ), has in the last few years become less and less lævorotatory ( $- 4^\circ$  to  $- 5^\circ$  have been observed). This behaviour would be explained by an admixture of African copaiba balsam. Balsams, whose oil rotates below  $- 7^\circ$ , should be rejected as untrustworthy.

With reference to these statements, Umney and Bennett<sup>2)</sup> point out that it is desirable to determine a maximum content of resin acids, in order to exclude adulterations with colophony, but at the same time to pay attention to the percentage content of volatile oil, which should be at most 50<sup>0</sup>/<sub>0</sub>. For the rotation of the oil, the authors propose  $- 5^\circ$  to  $- 25^\circ$  as limits of value.

**Coumarin.** C. E. Bradley<sup>3)</sup> reports on the presence of coumarin in *Achlys triphylla*. This plant, a Berberidacea, grows in large quantities in the pine forests on the Pacific coast of North America, to the West of the Cascade Mountains, and thriving especially in shady, swampy places, it forms there with its broad leaves a wide green carpet over extensive areas. Its common name is "wild vanilla". The young plants appear in April, and possess an extremely pleasant odour, particularly when quite young. After several unsuccessful attempts to isolate the odoriferous substance by distillation with steam, the author obtained, on extracting the leaves with ether, crystals of the m. p.  $65^\circ$ , which after further purification and recrystallisation from hot water, melted at  $67^\circ$ , and were found to be coumarin.

**Linalyl acetate.** In view of the high prices of bergamot oil, we would not fail to call attention to this speciality of ours, which has gained a constantly increasing number of admirers in the better-class perfumery trade. If it is taken into consideration that our product shows an ester-content of 80<sup>0</sup>/<sub>0</sub>, against 35 to 38<sup>0</sup>/<sub>0</sub> in natural bergamot oil, it is obvious that its use at the present market prices of bergamot oil is extremely advantageous. Furthermore the absolute freedom from colour is a further distinct advantage of linalyl acetate.

**Menthol.** With regard to this article, we can only refer to what we said on page 71 on the subject of Japanese peppermint oil. But

<sup>1)</sup> *Chemist and Druggist* **70** (1907), 521.

<sup>2)</sup> *Ibidem* **70** (1907), 569.

<sup>3)</sup> *Journ. Amer. chem. Soc.* **29** (1907), 606.

we must not pass over the interesting fact that in the course of the last few months menthol has constantly been quoted cheaper in London than in Japan, — no doubt the best proof that in Europe all confidence in a revival of the market has gone, and that there is an inclination to realise. The quotations were:

	in London (less $2\frac{1}{2}\%$ )	in Japan (net)
on 1 <sup>st</sup> May	8/3	8/6
1 <sup>st</sup> June	8/-	8/4 $\frac{1}{2}$
1 <sup>st</sup> July	8/-	8/1 $\frac{1}{2}$
1 <sup>st</sup> August	7/9	8/-
1 <sup>st</sup> September	7/2	7/6

**Musk, Tonquin.** As was to be expected, the firm tone with which the last season commenced last autumn, has under the influence of a brisk demand continued also during the summer months, and at the end of June the quotations moved up to the average of 315 taels.

The last parcels placed on the market consisted mostly of very small pieces, but in spite of this they fetched full prices. Even heavily adulterated parcels were willingly bought at over 310 taels per catty. For this reason it appears to us perfectly logical to expect also high prices during the season commencing in October/November.

The shipments of musk during the first half-year of 1907 were as follows: —

Year	Paris	London	New York	Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1907	622	36	270	37	965 <sup>1)</sup>
against:					
1906	580 <sup>2)</sup>	—	177	46	803
1905	278	73	330	40	721
1904	489	50	249	50	838
1903	616	122	312	134	1184
1902	568	125	295	99	1087
1901	419	134	254	71	878
1900	630	43	174	36	883

<sup>1)</sup> Of this, about 85% Tonquin, 15% Sawko, Tampi and Cabardine.

<sup>2)</sup> Comp. Report October 1906, 97, Note 1.

H. Zwaardemaker has obtained very remarkable results in his olfactometric experiments with muskone<sup>1)</sup>. He observed that various substances differ very considerably from each other in respect of their capacity for absorbing the muskone odour from an atmosphere saturated with muskone vapours, and that in some substances the acquired characteristic muskone odour in the course of time gradually changes into an odour which resembles more the musk-aroma. The further study of these occurrences was made with a solution of muskone in odourless myristic acid prepared by us at Mr. Zwaardemaker's request<sup>2)</sup>. The myristic acid contained 0,627% muskone. From this myristic acid possessing the muskone odour, Zwaardemaker made an olfactometric cylinder 4 inches long by 5/16<sup>th</sup> inch diameter. In order to test the behaviour of various substances towards the muskone odour, this olfactometric cylinder was connected with cylinders of the same size of porous porcelain, arc lamp carbon, ebonite, steel, iron, aluminium, silver, sulphur, tin, copper, nickel, glass, lead containing tin, and pure lead, and a uniform current of air (84 cc. per second) was passed through each during 5 minutes.

The tests with the various cylinders now showed that porcelain, carbon, and steel had acquired no muskone odour at all; that the other substances, and especially tin, copper, nickel, glass, and lead, showed a distinct absorption of odour which during the first few minutes and even hours had an undeniable muskone character, but gradually changed into one more like musk, until it finally resembled the musk odour completely.

This conversion of the odour-quality applies particularly to tin, copper, nickel, glass, glazed porcelain, lead containing tin, and pure lead.

An increase in the strength of the absorbed odour was also apparent, for example in the case of lead, the maximum occurring after three times 24 hours. In the course of time the substances examined lost the acquired odour again completely. But the various substances do not lose the odour with equal rapidity; thus, whilst iron loses the odour already in a few minutes, with lead this occurs only after 11 to 12 days. Similar experiments were then made with solutions of ionone and skatol, when it was found that these odoriferous substances behave in a manner different from muskone; ionone attaches itself principally to substances which do not absorb muskone at all — for example steel; skatol adheres best to aluminium, which shows only a feeble tendency to attract muskone.

<sup>1)</sup> According to reprints kindly sent us: "De absorptie van muscongeur tegen vlakten van verschillend materiaal". Koninklijke Akademie van Wetenschappen te Amsterdam 1907, 31, 139.

<sup>2)</sup> A solution of muskone in *Paraffinum liquidum* was found to be odourless.

No satisfactory explanation can yet be given of these occurrences, especially of the remarkable conversion of the muskone odour into musk odour.

Zwaardemaker believes that the adsorption of the odours and the conversion of the musk odour take place within the condensed air film which covers all surfaces. But the view that the odoriferous substances are absorbed by the metals themselves is also worthy of consideration.

These interesting observations of Zwaardemaker on the adhesibility of odours to metals and other substances deserve a further study. Not less important, though at present even less capable of explanation, appears to us the observation made by Zwaardemaker of the change in the odour-quality during the adhesion of the muskone odour to certain substances. The fact that in such cases the muskone odour changes into musk odour, appears to justify in the first instance the question as to what, according to Zwaardemaker, must here be understood by musk odour. According to our study of the odoriferous substances of natural musk, the natural musk odour is a mixed odour, which is brought about by the joint action of the muskone odour with other unpleasantly smelling substances of the musk-secretion. But it can scarcely be accepted that the muskone odour, while adhering to non-odorous surfaces, should come to resemble this mixed odour! However this may be, the fact itself is already important, that under certain conditions a pronounced change in the odour-quality, which is not due to greater dilution of the odoriferous substances, should occur at all.

**Peru balsam.** Numerous enquiries on the part of consumers induce us to point out that for the present there is no prospect of cheaper prices for this article, as the supplies remain scarce, and are barely sufficient for the current demand. The enormous increase in the prices is said to be due to this, that the Indians in the producing districts are afraid to bring the balsam into the towns, as they would expose themselves to the risk, owing to the warlike conditions in San Salvador and Guatemala, of being "pressed" into military service. There are also frequent reports that the exporters in the producing districts have come to an understanding with regard to the prices.

**Safrol.** Having made purchases in good time of large parcels of raw material, we were fortunately able to escape entirely the enormous prices of crude camphor oil quoted in May, and we have now only goods at our disposal which have been bought advantageously, and which we are consequently able to offer to the consumers at reduced quotations. For the rest, we would refer to our detailed information on camphor oil on p. 20 of the present Report, and would

only add that, in agreement with the position of the crude material, the prices of safrol may very shortly experience a further reduction. We would also once more call attention to the fact, that according to official information from the German Consul at Kobe<sup>1)</sup>, the manufacture of safrol in Japan itself has now been finally given up. Competition from that quarter is therefore no longer to be expected.

**Tannothymal.** Previous researches by Hildebrandt<sup>2)</sup> had shown that in benzyloxy piperidines the intensity of the (piperidine) action depends upon the structure of the benzene ring which by means of the methylene group is linked to the piperidine ring. The strongest action was shown by those derivatives in which, starting from the phenolic hydroxyl group, either the one ortho-position, or the para-position, or finally the two meta-positions adjacent to the methylene group, were unoccupied.

These observations led Hildebrandt<sup>3)</sup> to bring, instead of piperidine, a substance of known therapeutic value, i. e. tannin, in reaction with phenols and formaldehyde. In this manner it would be possible to arrive at remedies which could be used as astringents in the place of tannin, without possessing the latter's disagreeable properties (nauseous taste, and an action incommoding the stomach by precipitation of albumin). If the alcoholic solution of the components phenol, formaldehyde, and tannin is allowed, with stirring, to flow into concentrated hydrochloric acid as condensing agent, condensation takes place in this manner, that a hydrogen atom each of the phenol and tannin nuclei separate out with the oxygen of formaldehyde, with formation of water. In this way a large number of monohydroxyl phenols were condensed, including such which contain, in addition to a free hydroxyl, one or two "masked" i. e. alkylated hydroxyls. It is in each case possible to remove by washing with water the hydrochloric acid adhering to the condensation products, and to obtain well-pulverising substances. In their physiological examination it was found above all, that all those products whose phenol-rest contains one or more masked hydroxyls, such as the derivatives of guaiacol, eugenol, pyrogallol dimethyl ether, etc., not only develop no astringent tannin action, but on the contrary have an irritating effect on the intestinal canal. The taste of these products with the alkyloxy group is characterised by a disagreeable burning sensation. On the other hand, those derivatives which — like phenol itself — carry no further groups

<sup>1)</sup> See p. 20.

<sup>2)</sup> Arch. f. exper. Pharmakolog. **44** (1900), 278; Zeitschr. f. physiol. Chem. **43** (1904), 248; Liebig's Annalen **344** (1906), 298.

<sup>3)</sup> Arch. f. exper. Pharmakolog. **56** (1907), 410; Münch. mediz. Wochenschr. **54** (1907), 1219.

beyond the OH-group in the nucleus, or which in certain places have pure alkyl groups, possess the astringent action of tannin. In these cases the irritating action due to the presence of the phenol-rest is so slight, that it is not able to affect, in the alkaline intestine, the astringent action of the tannin components. The advantage of these derivatives over tannin is, however, due to this, that owing to their insolubility in acids they have no influence on the stomach, and on the other hand, thanks to the phenol components, are capable of developing in the intestine a special antiseptic action.

In view of his experience, Hildebrandt considers the thymol derivative of tannin as the most suitable substance for practical purposes, the more so, as thymol itself is the most harmless of all phenols, and has proved valuable for internal administration as an intestinal disinfectant and against certain intestinal parasites.

This preparation is manufactured by us, and placed on the market under the name Tannothymal (m. p. about  $235^{\circ}$ ). It is a yellowish-white to reddish powder, and is specially characterised by the fact that without impairing the astringent action of tannin, it is almost tasteless; that on the one hand, owing to its insolubility in acids, it does not cause any trouble whatever to the stomach, and on the other, is capable of being dissolved and split up in the alkaline intestinal juice, where the antiseptic thymol action can then develop. It is scarcely soluble in water, more readily in alcohol. In spite of the ready solubility of the difficultly resorbed compound in alkali, only a small proportion of the tannothymal administered internally enters into the general circulation, as was proved by the examination of the urine, so that the action can continue through the entire intestinal canal.

Tannothymal was tested by O. Baumgarten<sup>1)</sup>, Privatdocent at the University of Halle, with regard to its action in diarrhoea and intestinal catarrh. It was found to be an extremely reliable intestinal astringent in particularly obstinate cases, in which every other medication (tannigen, tannalbin, tannin and opium) failed, and it had at the same time a considerable antiseptic and a striking desodorising effect. The dose of tannothymal for adults is 1 g., to be taken in one dose, in case of need several times daily, for children proportionately less; in sick-fund practice it may be prescribed in quantities of a knife-point's to a tea-spoon full, three or more times daily.

Free samples of this new preparation and also literature are at all times at the disposal of medical practitioners.

**Thiosinamine.** Hagenbach-Burckhardt<sup>2)</sup> reports on two cases in which cicatricial strictures of the oesophagus were cured by

<sup>1)</sup> Münch. mediz. Wochenschr. 54 (1907), 1220; Klinisch-therap. Wochenschr. 1907, no. 28.

<sup>2)</sup> Mediz. Klinik 3 (1907), Nr. 27.

means of thiosinamine. The first case was that of stricture in a five years old child, caused by the accidental swallowing of concentrated caustic soda lye. Before the thiosinamine treatment, it was impossible to enter the stomach even with the finest probe; but after the second injection the cicatrised tissue had already become so much relaxed, that a flexible 3 mm. probe could be introduced. After the seventh injection even a  $9\frac{1}{2}$  mm. probe could enter without difficulty. The cure was complete. In the second case it was a question of a stricture caused by inadvertently taking concentrated potash lye, through which previous to the treatment only a  $2\frac{1}{2}$  mm. probe could pass. Here also, within a few days from the commencement of the thiosinamine treatment (injection of 1,0 to 1,5 in the skin of the back, in the vicinity of the spine), a relaxation of the cicatrised tissue became apparent, so that a 6 mm. probe could pass through it. An improvement in the general condition (cessation of vomiting, increase of appetite) continued, with a considerable increase in the weight of the patient, and finally a 10 mm. probe could easily pass the cicatrised place. Four months after the treatment commenced, the patient had completely recovered.

**Thymol.** No change has come into the prices of the raw material during the summer months, and the absolutely senseless price-cutting, which has now for a long time rendered the thymol business a source of disgust to every manufacturer with commercial ideas, continues unabashed. Although there has been no lack of attempts to raise the value of this article, the position of the crude material, as already stated, has not assisted these movements, and up to the present they have remained without result.

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## Notes on recent research work concerning terpenes and terpene derivatives.

### General.

Whilst the nowadays generally accepted formulæ for the principal terpene derivatives, such as camphor, pinene, and numerous other compounds, owe their origin and confirmation to the difficult work, extending over years and even decades, of many investigators, G. Wendt<sup>1)</sup> considers it his duty to draw up new formulæ for the whole of the terpene compounds, which he bases, without any experimental foundation, entirely arbitrarily, and with a sovereign disregard of all previous labour, upon a "pure" carbon atom, that is to say,

<sup>1)</sup> Pharm. Ztg. 52 (1907), 331.

a carbon atom combined in his opinion with four others. A simple reference to this publication with its 16 new formulæ, which may almost be called an insult to all the scientists working in the domain of the terpene chemistry, may suffice in this place.

O. Thiele<sup>1)</sup> discusses the possibility of producing essential oils from drugs and blossoms in the German Pacific colonies, especially in Samoa. So long as the crude material (of which particularly the leaves on account of their bulk, and the blossoms on account of their low keeping qualities, cannot stand a long transport) is not distilled on the spot, it is only possible, in view of the heavy expense, to export the most valuable material for the purpose of working up. For this reason Thiele proposes to arrange a simple portable distilling apparatus, or at least to improve for the blossoms the process, already crudely worked by the natives, of binding the aroma to cocoanut oil. The blossoms which come more particularly under consideration for the perfume industry, are the ylang ylang blossoms, whose mother-plant, *Cananga odorata*, is found in Samoa, and is already utilised by the natives; further, the blossoms of pua (*Gardenia* species), of the suni tree (*Drymispermum Burnettianum*), fala or fasa blossoms, fuemanogi and fuemaga (*Cestrum* species), mao (*Melochria odorata*) and others.

Of drugs which keep better and stand a longer transport, Thiele mentions the tuberous aromatic roots of mumuta grass (a species of *Andropogon*), the fruits of ifi-ifi (*Parinarium laurinum*) and laga'ali (*Agleia edulis*), the resins of the ma'foa and ma'ali trees, the leaves of togai (*Acronychia*), citrus species, and many others.

In a meeting<sup>2)</sup> of the "Société Nationale d'Horticulture de France" held on the 14<sup>th</sup> February 1907, Etienne Pétréano made the bold assertion that the constituents scientifically detected in certain natural blossom oils, such, for example, as methyl ester of anthranilic acid, benzyl acetate, and geraniol, are not at all present in the natural products in which they had been discovered. Thus, the treatise on the presence of methyl anthranilate in oil of orange blossoms, was only "a cleverly written publication, which had the appearance of scientific truth". But according to his own researches, orange blossom oil did not contain methyl ester of anthranilic acid, nor rose oil any trace of geraniol, or oil of jasmine blossoms any trace of benzyl acetate. An oil of orange blossoms which contains methyl anthranilate would therefore be adulterated.

<sup>1)</sup> Chem. Ztg. **31** (1907), 629.

<sup>2)</sup> Journal de la Soc. nat. d'Horticulture de France, February 1907.

As the methods for the detection of methyl ester of anthranilic acid, benzyl acetate, and geraniol, in blossom oils have been worked out accurately, and successfully employed by various authors, it is difficult to understand how Mr. Pétréano has managed not to find these bodies in his oils. But as he does not say how he has made his experiments, nor what he has actually found in them, it is not worth while to waste another word on this chemical performance and the conclusions drawn from it.

J. Enklaar<sup>1)</sup> has extended the hydrogenation method of Sabatier and Senderens (reduction with metallic powders in a current of hydrogen) to aliphatic compounds with several double bonds, such as ocimene, geraniol, linalool, citral, etc. The hydrocarbons yielded the corresponding saturated bodies, the alcohols either the corresponding hydrocarbons, or saturated aliphatic alcohols. In the case of linalool this conversion was accomplished at a temperature of 130 to 140°. Citral yielded in addition to the expected aliphatic, a series of cyclic compounds, amongst which an alcohol resembling the menthol of peppermint oil. According to Enklaar's experiments, copper is more suitable for this method than nickel. With regard to the reaction-mechanism, the author is of opinion that the metal does not combine chemically with the hydrogen, but absorbs it.

### Bibliographical Notes.

Of Semmler's text-book „Die ätherischen Öle, nach ihren Bestandteilen, unter Berücksichtigung der geschichtlichen Entwicklung“ (The essential oils, according to their constituents with regard to the historical development), to the first numbers of which we have already called attention in our Report of October 1905, p. 86, the final number appeared at the end of June of this year. At the time we gave our opinion on the general part of this work, which has appeared in four stout volumes containing about 2700 pages of text. The special part contains in three volumes the principal sections: methane derivatives, hydrated cyclic compounds, and benzene derivatives. In each of these principal chapters are described, in the same sequence, the hydrocarbons, alcohols (phenols), aldehydes, ketones, acids, oxides, the several classes of bodies containing sulphur and nitrogen, — first of all the saturated, and then the unsaturated members of each series. Of each body there are treated in detail, its occurrence, isolation, possible synthesis; physical, physiological (pharmacological as well as odoriferous) and chemical properties, in which latter a distinction is made between chemical changes due to physical and those due to

<sup>1)</sup> Chem. Weekblad 4 (1907), 322. Accord. to Chem. Zentralbl. 1907, II. 56.

chemical action; finally, identification, constitution, isolation, and history. To those who are interested in the historical side of this domain, the constantly emphasised relationship of the individual, genetically closely allied members, and the very numerous references to the literature on the subject, which go back to the very commencement of chemical work, may particularly possess lasting value. Whoever wishes to be scientifically informed on a constituent of an essential oil, its occurrence in nature, in other oils, its production, constitution, the history of its investigation, finds an abundance of material in this work of an author, who has already been known for a long time as a successful investigator of the domain of the terpenes.

The essential oils themselves are considered in so far, as in every compound discussed occurring in Nature, the individual mother plants, their families, and the oils containing the compound in question are mentioned. A table arranged according to the families of the plants also gives information on the plants and the individual parts thereof which come under consideration for the production of essential oils. In compiling the very voluminous material, which has been treated with typical thoroughness, the author was not, as in the case of other works, guided by practical requirements to deal with the oils as such; his leading idea was to give a description of the components of the various oils more for the purpose of research work.

Brandel<sup>1)</sup> continues abstracting (to which we have repeatedly referred) the publications in the domain of the terpene chemistry in the course of the year 1905. Up to the present he has, in the order of Gildemeister's and Hoffmann's work, dealt with the oils up to those of the Myrtaceæ.

### Analytical notes.

In a previous Report<sup>2)</sup> we have already referred to the cryoscopic method for determining the essential oil in spices, etc., worked out by Beckmann and Danckwortt; we now return to this, as a more detailed treatise on the subject by Beckmann<sup>3)</sup> has made its appearance. Ethylene bromide, which possesses a sufficiently high molecular depression  $K = 118^\circ$ , and solidifies at  $+8^\circ$ , was found to be the best solvent. It is desirable to mix the ethylene bromide, before determining its freezing point, by way of trial with a few drops of water, and also to submit the solution prepared with dry ethylene bromide to the same test only after a few drops of water have been

<sup>1)</sup> Pharm. Review 25 (1907), 64, 121.

<sup>2)</sup> Report October 1906, 104.

<sup>3)</sup> Arch. der Pharm. 245 (1907) 211.

added, as it is difficult to dry a preparation always to exactly the same degree, and the freezing point falls by  $0,15^{\circ}$  if dry ethylene bromide is mixed with a few drops of water. In examining spices, the process is as follows: 5 g. of the ground spice or drug are left standing with 30 g. anhydrous ethylene bromide for one day, and the solution filtered through cotton wool in the freezing tube. To the solution, which has a yellow to green colour, and need not be absolutely clear, a few drops of water are then added, and it is brought to congeal. The temperature of the freezing bath is kept at  $5$  to  $6^{\circ}$ . The depression is represented by the difference between the freezing temperature of the solution, and that of the moist ethylene bromide. The depression-values may be useful for identifying drugs.

In order to ascertain separately the depression-value of the volatile portions (essential oils) which during the extraction pass over into the ethylene bromide, the most suitable way is to drive them off with steam (using a separate sample for this purpose), and after extracting the residue with ethylene bromide, to ascertain by a fresh determination of the freezing point, the depression-value of the volatile substances as the resulting difference. If the depressions produced by pure essential oils in moist ethylene bromide are determined, the content can at once be calculated from the result, for the depressions are proportionate to the contents.

With a view to reducing the resulting depressions to a uniform standard, the specific depression is calculated, i. e. the depression which one gram of the dissolved substance would produce in 100 g. solvent. If 30 g. ethylene bromide are always used, the specific depression

is  $C = \frac{0,3 \Delta}{s}$ , in which  $\Delta$  represents the depression observed,  $s$  the

number of grams of the substance dissolved in 30 g. ethylene bromide. The molecular weight of the substance in question is then

$M = \frac{K}{C}$  ( $K$  = molecular depression). If 5 g. of the spice contain  $s$

grams essential oil, the percentage is  $20 s$ ; on the other hand

$s = \frac{0,3 D}{C}$ , and the percentage therefore  $= \frac{6 D}{C}$ , in which  $D$  means

the difference in the depressions of the extract of the distilled and the non-distilled sample.

The estimation of essential oils in aromatic waters is carried out thus: 250 g. aromatic water are strongly agitated in a separating funnel with 30 g. ethylene bromide of a known freezing point in the moist state. After separation, the freezing point is ascertained. For 250 g. water,  $0,03^{\circ}$  depression must be deducted, as, owing to the solubility

of ethylene bromide in water, the depressions obtained are too large in consequence of the increased concentration.

If waters containing alcohol are extracted with ethylene bromide, the alcohol passes over in the latter, and would increase the depression. This error can be corrected if the ethylene bromide containing alcohol is once more shaken with 250 g. pure water. The ethylene bromide thus remaining can now be used at once for the determination of the freezing point. If the extraction is repeated again with 250 g. water, the freezing point will fall by the correction-standard of  $0,03^{\circ}$ , as soon as the ethylene bromide solution is completely freed from alcohol.

In checking Vaubel's<sup>1)</sup> method for the determination of the bromine number in essential oils, G. Mossler<sup>2)</sup> found that the reaction does not proceed sufficiently rapidly to obtain reliable figures. But in spite of the unsatisfactory results, he has occupied himself further with the question of the action of bromine on essential oils, and has worked out a method which renders it possible to determine the whole quantity of the bromine which has reacted, and the portion converted into hydrobromic acid. In order to determine the bromine number (i. e. the quantity of bromine used up by an essential oil, expressed in per cent.), Mossler proceeds as follows: On the oil dissolved in carbon tetrachloride he allows bromine to act which is evolved from a solution of potassium bromide-bromate by acidification. When the action has proceeded for six hours, he mixes the liquid with solution of stannous chloride, until it is completely decolorised, and determines the excess of stannous chloride with the help of decinormal iodine solution.

In order to determine the quantity of hydrogen bromide formed during the action, Mossler also proposes to follow first the method previously indicated. But when the time for reaction has elapsed, he adds a solution of potassium bromate, shakes the mixture strongly, and filters the aqueous layer in a separating funnel. From this solution also the bromine is removed by extracting it three times with carbon tetrachloride; to 100 cc. of the filtrate is now added potassium iodide, and the iodine separated out is determined with solution of sodium thiosulphate. With regard to the blind tests which should be made at the same time, and also to the calculation, we would refer to the original work. The quantity of bromine which is converted into hydrogen bromide, expressed in per cent. of the oil, Mossler designates as the hydrobromic acid number. It is claimed that from the relation between the bromine number and the hydrobromic acid number, the adulterations of the oils can be recognised.

<sup>1)</sup> Comp. Report April 1906, 66; October 1906, 77.

<sup>2)</sup> Zeitschr. d. allg. österr. Apoth. Ver. 45 (1907), 223, 235, 251, 267, 283, 299.

We consider the determination of such indices for judging the value of essential oils, as less correct, and unnecessary, as a sufficient number of unobjectionable constants is already taken into consideration in the examination. The physical constants (specific gravity, rotatory power, index of refraction, solubility) which can be easily and rapidly determined, give in most cases sufficient information as to the quality of the oils. If, in addition to this, serviceable methods of examination are carried out for the purpose of quantitatively estimating individual constituents or groups of compounds, such generalised methods as the determination of the bromine number are superfluous, the more so as the compounds which enter into reaction with the bromine are not always known. It is desirable that the chemical methods of tests are adapted to the peculiarity of the individual oil, and that the investigators who occupy themselves with the working out of such methods, concentrate their work upon discovering exact methods for the direct determination of some important constituent of the oil, or of the groups of bodies present in it, such as are, for example, at our disposal in the saponification for the ester-determination, in the acetylation for the estimation of the alcohols, in the bisulphite method for the determination of aldehydes, and the like, some of which are still open to improvement by suitable modifications.

With regard to our own results with Mossler's method which we have submitted to a test on eucalyptus oil, see under Eucalyptus oil, p. 50.

**Hydroxyl determination.** The behaviour of hydroxyl compounds towards magnesium organic compounds has induced Tschugaeff<sup>1)</sup> to make use of magnesium-methyl iodide as a reagent on the hydroxyl-group. As in this reaction one molecule methane is formed to every hydroxylic hydrogen atom, Hibbert and Sudborough<sup>2)</sup> endeavoured to work out on this basis a quantitative method for the determination of hydroxyl groups in organic compounds. By using amyl ether as solvent for the magnesium organic compounds, and allowing the reaction to be accomplished in a nitrogen atmosphere, they obtained in a few cases satisfactory results, but in other cases the method failed, probably owing to the insolubility of the substances in question in the amyl ether.

Th. Zerewitinoff<sup>3)</sup> has now occupied himself in improving this method, and he obtained good results by it, also when using amyl ether as solvent for the substance to be examined. As a generally applicable solvent he recommends pyridine, from which the water must

<sup>1)</sup> Berl. Berichte **35** (1902), 3912; Report April 1903, 88.

<sup>2)</sup> Proceed. chem. Soc. **19** (1903), 285. Chem. Zentralbl. **1904**, I. 402.

<sup>3)</sup> Berl. Berichte **40** (1907), 2023.

be thoroughly removed (distilled and kept over barium oxide). According to Oddo<sup>1)</sup>, pyridine forms with magnesium organic compounds peculiar complexes; yet the compound  $(C_5H_5N)_2 \cdot IMgCH_3 \cdot O(O_5H_{11})_2$  which separates out when a solution of  $CH_3MgI$  in amyl ether is mixed with pyridine, reacts with bodies containing hydroxyl in the same manner as free  $CH_3MgI$ . When using pyridine the determination must be carried out at ordinary temperature, and the volume of gas must be read off as quickly as possible, as soon as the temperature in the apparatus is again brought to the initial temperature, as otherwise the pyridine also enters into reaction, with evolution of gas.

The determination is carried out in an apparatus which consists chiefly of a cylindrical reaction-vessel provided with a lateral bulb, and a gas-measuring apparatus resembling Lunge's nitrometer. The apparatus and reagents must be absolutely dry. 0,03 to 0,2 g. of the substance (according to the molecular weight and hydroxyl number) are dissolved in about 15 cc. solvent in the reaction-vessel; now by means of a special funnel 5 cc. of the magnesium organic compound (in solution) are placed in the bulb in which not a drop of the first-named solution may have entered, and the vessel is tightly closed by connecting it with the measuring apparatus. In order to obtain the proper temperature, the apparatus is immersed in water. After atmospheric pressure has again been restored in the apparatus, and the gas-collecting tube has been filled with mercury, the methylmagnesium iodide is mixed with the solution of the substance to be examined, by allowing the contents of the bulb to flow into the cylindrical portion of the apparatus; at the same time the connection is made with the collecting tube by turning the cock in a suitable position. When the reaction-vessel is strongly shaken, a brisk evolution of gas takes place. As soon as the volume of gas no longer increases, the vessel is again put in the water-bath so as to obtain the original temperature, when a contraction of volume takes place. If pyridine is used as solvent, the volume must be read off immediately the contraction ceases, as otherwise a continuous, though slow, increase of the volume of gas takes place. For calculation, the minimum should always be taken. If amyl ether is used, the volume of gas does not alter once the temperature is constant.

Simultaneously with the determination of the volume, the temperature of the gas and the barometric pressure are noted. If pyridine is used, 16 mm. must be deducted from the atmospheric pressure observed, as this represents the vapour-tension of pyridine at 18°. If amyl ether is employed, its vapour-tension at ordinary temperature may be neglected.

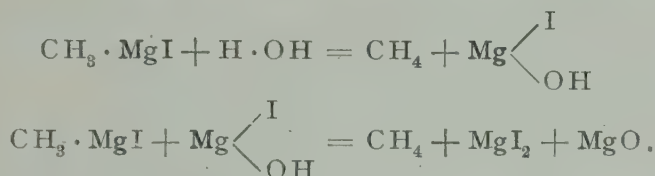
<sup>1)</sup> Chem. Zentralbl. 1904, II. 836.

The percentage of hydroxyl-groups is calculated according to the formula

$$x = \% \text{ OH} = \frac{0,000719 \cdot V \cdot 17 \cdot 100}{16 \cdot S} = 0,0764 \frac{V}{S},$$

0,000719 being the weight in g. of 1 cc.  $\text{CH}_4$  at  $0^\circ$  and 760 mm. pressure, 16 the molecular weight in g. of  $\text{CH}_4$ , 17 that of  $\text{OH}$ ,  $V$  the volume of the  $\text{CH}_4$  separated off, reduced to  $0^\circ$  and 760 mm. pressure, and expressed in cc.,  $S$  the weight in g. of the substance to be examined.

In the case of compounds containing water of crystallisation, it is necessary to calculate the percentage of active hydrogen, as both hydrogen atoms of the water enter in reaction with methyl magnesium iodide.



For calculating the percentage of active hydrogen, the formula

$$y = \% \text{ H} = \frac{V \cdot 0,000719 \cdot 100}{16 \cdot S} = 0,00449 \frac{V}{S}.$$

is employed.

Although the magnesium organic compounds are attacked by the oxygen of the air, these determinations can be carried out in an atmosphere of air; at any rate, Zerewitinoff obtained no essentially different results, when he filled up the apparatus before carrying out the experiment with an indifferent gas (nitrogen or methane).

If in the case of acids the results of this hydroxyl-determination are combined with the results of the titration, all data are obtained for the calculation of the basicity and atomicity of the acid in question.

Whether Zerewitinoff's process can also be employed for the valuation of essential oils, in which frequently compounds containing hydroxyl are met with, is a question which can only be solved by further experiments.

Linalool determination according to Boulez. On the occasion of a discussion on the linalool-content of linaloe oils, Simmons<sup>1)</sup> on the one hand, and Parry and Bennett<sup>2)</sup> on the other, advance their views on the determination of linalool according to Boulez, which we have discussed in detail in our last Report (page 120).

Simmons, who himself has carried out several unsuccessful attempts to determine linalool, commits in a check test of Boulez's method the same error in the calculation as Boulez himself, and thereby also obtains apparently very good results. Parry and Bennett, on the

other hand, have made the same experience as we in checking this method, and they also come to the conclusion that the linalool determination carried out according to Boulez, does not give reliable results.

In connection with what we said in our last Report on the subject of Boulez's method, we would now summarise our opinion on this matter as follows: with terpeneol, under suitable conditions, the results obtained are satisfactory; but the accuracy with regard to the linalool determination still leaves very much to be desired, although it must be admitted that the results are much better if a diluent is used, than if the undiluted oil is acetylated. It remains to be seen whether the process can also by suitable modifications be rendered useful for the determination of linalool.

With regard to the determination of cineol in eucalyptus oils, see under the heading Eucalyptus oil, p. 45.

For the determination of aldehydes and ketones, P. B. Rother<sup>1)</sup> has worked out a new method. It is based on this, that aldehydes and ketones are converted in phenyl hydrazones by adding definite quantities of free phenyl hydrazin, the excess of phenyl hydrazin added is brought into reaction with iodine, and the iodine not used up is then titrated with thiosulphate solution. According to E. Fischer, iodine acts on phenyl hydrazin according to the equation: —



But in the presence of an excess of iodine, the reaction, according to E. v. Meyer, takes place as follows: —



After experiments made by Rother with the view of detecting possible sources of error, and which were made with reference to changes in the standard of the phenyl hydrazin solution during the time of testing, the influence of alcohol on the iodine starch reaction, and the iodine action on the hydrazone formed, etc., the author finally gives the following directions for carrying out the determination: —

5 g. (fully) phenyl hydrazin are weighed out, dissolved in about 250 cc. warmed water, filtered in a 500 cc. flask for removing resinified products, and filled up to the mark, after cooling, with boiled distilled water. The solution keeps badly, and must be kept well-closed and protected from light.

<sup>1)</sup> According to a thesis kindly sent to us: Die Bestimmung der Aldehyde und Ketone zur Bewertung ätherischer Öle (The determination of aldehydes and ketones for the valuation of essential oils). Dresden, 1907.

The standard of the phenyl hydrazin solution is determined as follows: in a flask of one litre capacity are placed about 300 cc. water and exactly 40 cc. decinormal iodine solution. Next, 10 cc. of the phenyl hydrazin solution are allowed to flow from a burette in a small flask containing about 50 cc. water, and the contents are gradually added, while strongly shaken, to the litre flask. After about 1 minute, it is titrated back with decinormal thiosulphate solution; 0,1 g. pure phenyl hydrazin corresponds to 37 cc. decinormal iodine solution.

Of the substances to be tested, 0,5 to 1,0 g. are weighed off in a weighing glass, and in order to avoid oxidation a few cc. alcohol are added immediately. The content of the weighing glass is then washed with about 30 cc. alcohol in a quarter-litre flask, and so much of the phenyl hydrazin solution is now allowed to flow in, that 1 mol. phenyl hydrazin is present to every mol. of aldehyde (or ketone). The mixture is then repeatedly strongly shaken, and left standing for about 15 hours, protected from light, and with occasional shaking. It is then diluted with water, and filtered through a folded filter (if the liquid is not clear some plaster of Paris is added) into a litre flask containing about 500 cc. water and 10 to 20 cc. decinormal iodine solution, according to the quantity of phenyl hydrazin employed. During the filtration it is necessary to agitate frequently. The filter is well washed with water, and then the liquid, after adding some starch solution, is titrated back with decinormal thiosulphate solution.

The percentage  $x$  of aldehyde or ketone respectively is then calculated according to the formula:  $x = \frac{d \cdot M}{100 \cdot 4 \cdot s}$ , in which  $d$  represents the difference between the cc. decinormal iodine solution corresponding to the phenyl hydrazin used, and those used up during the test;  $M$  the molecular weight,  $s$  the quantity of the substance used in grams.

Of oils with a very low content of aldehydes (lemon oil), about 10 g. are used for the analysis; after the reaction with phenyl hydrazin they are separated in a separating funnel, and the titration only takes place after repeated washing of the non-aldehydic portions. In such case the samples analysed must be thoroughly shaken for a long time, and left standing for about 20 hours.

We were particularly interested in this Rother's process, as the author also recommends it specially for the determination of citral in lemon oil. For this reason we carried out check-tests, for which we used mixtures of perfectly fresh pure citral with pinene and limonene. It was then found that on the whole this method gives reliable results, but that it has not, in respect of accuracy, any considerable advantage over the volumetric bisulphite method and the sulphite method; for practical use in technical work the new method

is not to be preferred to the two above-mentioned methods, as owing to the bad keeping qualities of the required solutions, it is much too complicated, and takes too much time before the result of the examination is known. For the special purpose of the citral-determination in lemon oil, the method is not reliable enough, to judge the quality of the oil directly from the citral-content; the differences found by us are so large, that judging from the citral-determination alone, greatly adulterated oils might still be passed as satisfactory.

The result of our examinations may follow here:

In a mixture containing	40%	citral, we found	39,35%
" " " "	20%	" " "	18,93%
" " " "	5%	" " "	4,47%
			and 4,86%.

In a lemon oil whose citral-content had been determined by Rother as 5,5%, we found 6% and 5,22% respectively.

Now if we assume that the citral-content of lemon oil fluctuates between 3 and 5% and the results obtained by Rother's method are 0,5% too low, an oil with 2,5% citral (according to Rother) should, under such circumstances, be allowed to pass, although it might possibly have been produced by mixing a lemon oil containing 5% citral with say 60% terpenes. But such a coarse adulteration could without question be detected solely by the methods of examination hitherto in use.

For the detection or identification of certain bodies, such for example as oxygen, carbonic oxide, hydrogen cyanide, etc. the blood-spectrum has now been used for a long time, by observing the changes in the spectra called forth by these bodies. P. Bruylants<sup>1)</sup> now has recently made use of the spectroscopic behaviour of blood for the detection and the quantitative determination of aldehydes, and also for distinguishing them from ketones.

During the study of the action of various reducing agents on oxyhæmoglobin he had an opportunity of observing a reliable spectral reaction of hæmoglobin which is set up by aldehydes but not by ketones.

If to an approximately 4 per cent. solution of defibrinated blood is added yellow ammonium sulphide and a small quantity of aldehyde a reaction is rapidly accomplished, which is recognised by the peculiar spectrum and the brown coloration of the blood solution. The two absorption lines ( $\alpha$  and  $\beta$ ) of oxyhæmoglobin ( $\alpha$  tho the right of the line D, maximum of the absorption at  $\lambda$  580;  $\beta$  near the line H maximum of the absorption at  $\lambda$  540) first of all diminish in intensity

<sup>1)</sup> Bull. de l'Acad. roy. de Belgique (Classe des sciences) No. 3, 1907, 217  
Annales de Pharmacie 13 (1907), 321.

next a third line appears gradually between the two, and becomes more and more pronounced, so that at a given moment of the reaction three absorption lines of equal intensity can be observed. Subsequently the line  $\beta$  appears to become displaced towards the right; soon afterwards  $\alpha$  has entirely disappeared. There remain finally two absorption lines, a very distinct one on the left, and a diffuse one on the right. The appearances are somewhat different if the blood solution is previously reduced by polysulphides of ammonium. In such case only the one line of the reduced hæmoglobin is visible, which gradually becomes denser, and forms then the above-mentioned left line, whilst the diffuse line is formed on the right; this is the characteristic spectrum of hæmochromogene; the centre of the intense line is at  $\lambda$  560, that of the other diffuse and broader line at  $\lambda$  520. The position of the absorption lines is always the same, whatever aldehyde is used, but their width and intensity depend upon the quantity of the aldehyde added.

If under the last-mentioned conditions a ketone is employed instead of an aldehyde, only the reduced hæmoglobin absorption spectrum will be observed. The spectrum of the aldehyde compounds follows that of hæmochromogene. Of aldehydes which contain, besides the aldehyde-group, also other reactive groups, some are without action on hæmoglobin, whilst others give the above reaction.

The reaction of aldehydes on hæmoglobin is very reliable and sensitive. For example, in order to produce the reaction with 2,5 cc. reacting blood<sup>1)</sup>, 0,00039 gram citral are sufficient. Equal quantities of an aldehyde act in the same length of time always with equal intensity; on the other hand, the intensity and the commencement of the reaction are always proportionate to the reacting quantities of aldehyde. Bruylants has often found these conditions confirmed during the action of citral on hæmoglobin, and has in consequence worked out on this basis a method for the quantitative determination of citral in lemon oil, which is said to give satisfactory results. We will return to this method when the further publications promised by Bruylants have come to hand.

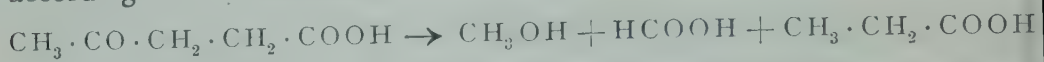
### Physical notes.

Some years ago Ciamician and Silber showed that acetone in aqueous solution is split up hydrolytically, by the action of light, into acetic acid and methane: —



<sup>1)</sup> This is obtained by adding to 19 cc. of a 3,7 per cent. solution of defibrinated pig's blood 1 cc. ammonium sulphide.

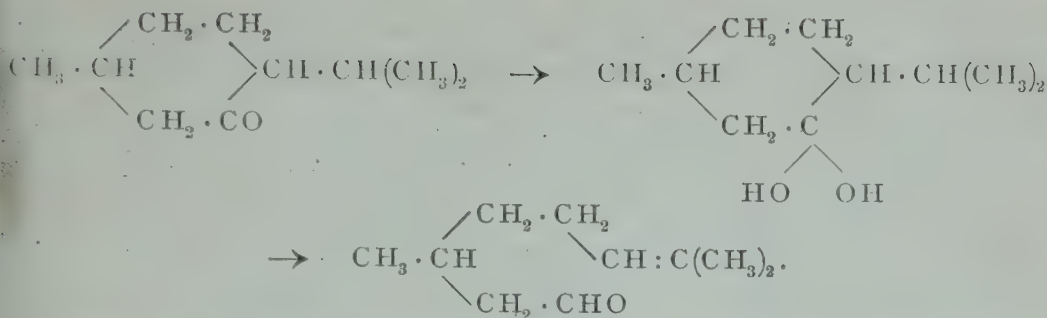
The authors have recently proved<sup>1)</sup> that methyl ethyl ketone is also split up, in an analogous manner, into acetic acid and ethane, and not (as might have been equally possible) into propionic acid and methane. Lævulic acid, that is to say a ketonic acid, should in an analogous manner be split up into a mixture of acetic and propionic acids, but only the acids propionic acid and formic acid, formed according to the reaction



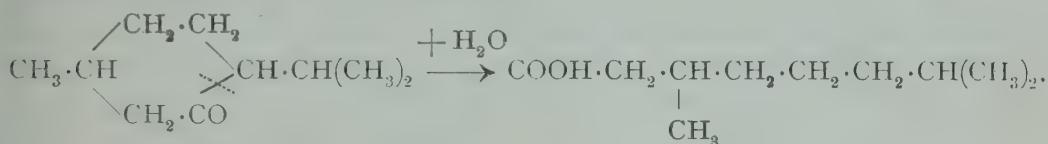
could be detected, and the formation of methyl alcohol was rendered probable. At any rate, only traces of methyl alcohol could be detected by oxidation to formaldehyde and by treatment of the repeatedly distilled first portions with hydrogen iodide according to Zeisel. When the silver salts of the acids were produced, the precipitate became deeply blackened during recrystallisation from water, which pointed to the presence of formic acid. The purified silver salts gave numbers which agreed well with propionic acid. In alcoholic solution the lævulic acid was partly reduced to  $\gamma$ -hydroxy valeric acid which occurred as lactone; another portion was esterified. From the alcohol there was formed partly acetaldehyde, corresponding to the reduction of the acid. A remarkable fact was the splitting up of menthone, with which, as a cyclic body, no splitting up of the molecule could be expected, but only an opening of the ring. Aqueous-alcoholic solutions of menthone (altogether 260 g. ketone, 975 cc. alcohol, 520 water) which had been exposed to the light during the summer and autumn months, separated off a layer of oil on the surface, and showed an acid reaction. The solution neutralised with soda, when extracted, yielded besides unchanged menthone, an aldehyde which imparted to the solution a peculiar odour, and which could be separated off from the menthone with bisulphite. From 160 g. d-menthone 11.5 g. aldehyde of the b. p. 193 to 197° were obtained; after further purification through the bisulphite compound, the body boiled absolutely constantly at 195°.

The combustion led to the formula  $\text{C}_{10}\text{H}_{18}\text{O}$ , that is to say, an isomeride of citronellal; but the two aldehydes were not identical, as the new aldehyde yielded a semicarbazone of the m. p. 88 to 89°, and citronellal one of the m. p. 81 to 82°. The hydroxamic acid of the aldehyde melted at 108 to 109°. Ciamician and Silber assume that the body is the mentho-citronellal produced by Wallach from mentho-citronellol (obtained by splitting up menthone oxime), whose semicarbazone also melts at 89°. The conversion would be accomplished as follows: —

<sup>1)</sup> Berl. Berichte 40 (1907), 2415.



In the neutralized aqueous-alcoholic solution there was present the sodium salt of an acid (from 100 g. menthone 10,7 g.) which boiled at 17 mm. pressure between 149 and 158°, at ordinary pressure from 249 to 252°. On analysis it proved to be a decylic acid, probably formed according to the formulæ: —

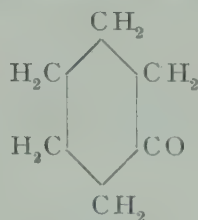


### Pharmacologico-physiological notes.

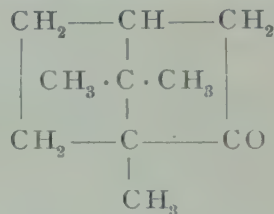
In the same manner as Witt's theory has established the relations between the chemical constitution and the dyeing properties of bodies, it has been attempted to explain the relationship between chemical constitution and odour. During the last few years, research has turned to the study of the relations existing between constitution and pharmacological action, and has found a number of analogies and laws. The results obtained up to the present have been summarised in a uniform manner by H. Hildebrandt, Privatdocent at the University of Halle, in a work now in the press: *Neuere Arzneimittel. Auf Grund von Studien über Beziehungen zwischen chemischer Konstitution und pharmakologischer Wirkung unter Berücksichtigung der synthetisch hergestellten Arzneimittel* (Modern pharmaceutical remedies. On the strength of studies on the relations between chemical constitution and pharmacological action, with regard to the synthetically-produced pharmaceutical remedies). (Leipzig, 1907, Akad. Verlagsgesellschaft.) After a short discussion of the difference in the action exerted biologically and pharmacologically by bodies chemically identical but differing physically, and by chemically isomeric, closely allied substances, the author turns to the discussion of the physiologico-chemical processes on which the action of the substances introduced into the organism is based, the influence of substitution, isomerism, and also the introduction of certain atomic groups. The following are dealt with in detail: the entry of atomic groups in

aniline derivatives and in hydrated bases, the physiological importance of the hydroxyl and carboxyl groups, and their etherification or esterification; the influence on the actions of compounds with an imido-group by the introduction of atomic complexes; the importance of the introduction of alkyl groups (attachment to O-, C-, N- and metallic atoms); the influence of pentavalent nitrogen, of nitriles, and of metal-organic and halogen-substituted compounds. Of special interest is the chapter on compounds of the camphor series, which forms part of our own particular domain, and which we quote here with the kind permission of the author and the publisher.

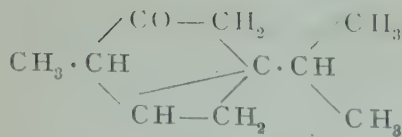
In discussing the three simple ring-ketones pentanone, hexanone and suberone, attention was called to the fact that the action stands in a definite relation to the size of the ring. It finds expression in a central paralysis and a paralysing action on the motoric nerve terminations<sup>1)</sup>, increasing with the size of the ring. Closely allied to hexanone are the compounds of the camphor series known as ketones:



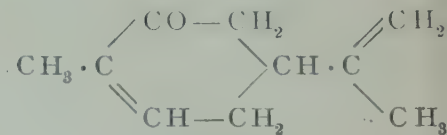
Hexanone



Camphor



Thujone



Carvone

To camphor belong two remarkable actions, a spasm-exciting action and an action on the heart, which exerts such an irritation on the latter that the muscarin-suspension of the frog's heart is counteracted<sup>2)</sup>, and in warm-blooded animals the blood-pressure is considerably increased<sup>3)</sup>, even when the vascular nerve centre has been paralysed by chloral hydrate. The same action is shown by monobromo camphor, camphorol, the oxidation product formed in the organism, and thujone<sup>4)</sup>, the active principle from the oils of the branches

of *Thuja occidentalis* L., whilst the hydroxycamphor  $\text{C}_8\text{H}_{14}$   $\begin{array}{l} \text{CHOH} \\ | \\ \text{CO} \end{array}$

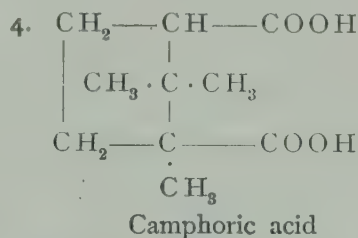
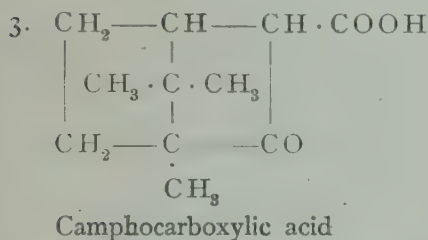
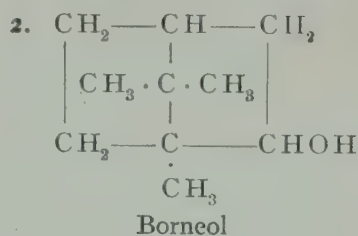
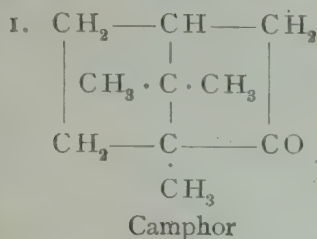
<sup>1)</sup> Jacobj, Hayashi, Szubinski, Arch. f. exp. Pharmacol. **50** (1903).

<sup>2)</sup> Harnack and Wittkowski, Arch. f. exp. Pharmacol. **5** (1876).

<sup>3)</sup> Wiedemann, Arch. f. exp. Pharmacol. **6** (1877).

<sup>4)</sup> H. Hildebrandt, Arch. f. exp. Pharmacol. **48** (1902).

obtained by reduction from camphor quinone  $C_8H_{14} \begin{matrix} \diagup CO \\ | \\ \diagdown CO \end{matrix}$ , and likewise borneol, do not show the action. In borneol, the carbonyl-group of camphor is converted in the alcohol-group.



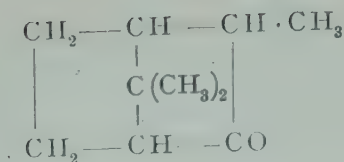
In camphocarboxylic acid (3), formed from camphor by the introduction of a carboxyl-group, the specific camphor-action is annulled. With regard to the action of camphoric acid (4), obtained from camphor by oxidation with nitric acid, the results of new researches by J. Fujitani<sup>1)</sup> have been published: it is just without those actions which are characteristic of the substances of the camphor-group, namely the paralysing action on the motoric nerve terminations and the spinal cord in frogs, and the irritating action on the convulsion-centre of warm-blooded animals; on the frog's heart, camphoric acid had rather an enfeebling action. The actions which it has in common with some substances of the camphor-group, are those on the respiratory centre, the peripheric vessels, and the heart of warm-blooded animals (Fujitani).

It was thought that the peculiar action of camphor was connected with the propylidene group inserted into the ring, which leads to the formation of a double-ring. But the behaviour of thujone, which agrees fairly well with that of camphor, shows that this assumption is unfounded. The reference to fenchone, in which a position of the methyl-group differing from that in camphor was assumed, does not alter this. The action of fenchone does not agree at all with that of camphor<sup>2)</sup>. Wallach<sup>3)</sup> has designated his formula indicated at the time for fenchone, as a provisional one.

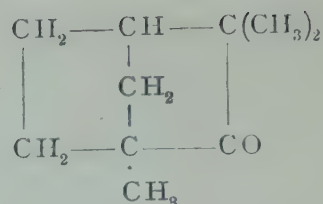
<sup>1)</sup> Arch. internat. de Pharmacodyn. **16** (1906), 273.

<sup>2)</sup> R. Matzel, Arch. internat. de Pharmacodyn. **24** (1906).

<sup>3)</sup> Liebig's Annalen **353** (1907), 209.

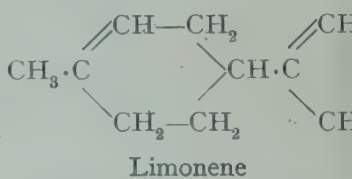
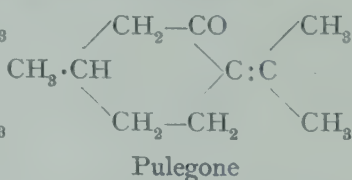
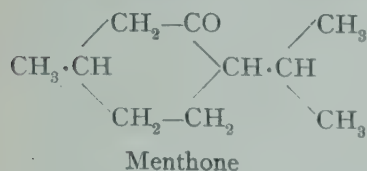


Fenchone formula  
according to Wallach



Fenchone formula  
according to Semmler<sup>1)</sup>.

Nevertheless, the presence of a "bridge-bond" appears to be necessary for bringing about the specific camphor-action; for carvone, in which a double linking is present in the nucleus, shows already considerable deviations from camphor in its physiological action; with the rabbit, the toxic effect, characterised by uninterrupted convulsions, is governed by an early occurring state of unconsciousness<sup>2)</sup>. The oxidation-product obtained by Harries<sup>3)</sup> from carvone on prolonged shaking with barium hydrate in the presence of oxygen, by absorption of one atom of oxygen, has an action not inferior to that of carvone; in the organism, the oxidation of carvone probably takes place, in the same manner as that of camphor, at a different place of the molecule. The fact that the convulsion-producing action of carvone is connected with the presence of the double linking in the nucleus, is clear from the behaviour of menthone and pulegone.



If in carvone, instead of the two double linkings, the attachment of two hydrogens each, and also another position of the CO-group is assumed, we arrive at menthone, which has not by far the same toxic action as carvone. Pulegone also, with a double linking in the isopropyl side-chain, does not possess the convulsion-exciting action of carvone, but has a chronic action on the parenchymatous organs, which leads to a considerable fatty degeneracy<sup>4)</sup>. The slight toxicity of the terpene limonene also proves that the presence of the carbonyl group is necessary for producing the action of carvone. From pulegone there is formed, by the action of sodium in alcoholic solution, pulegol, with the alcohol-group  $\text{CHOH}$  instead of the ketone-group; it consequently stands to pulegone, as borneol to camphor. But while

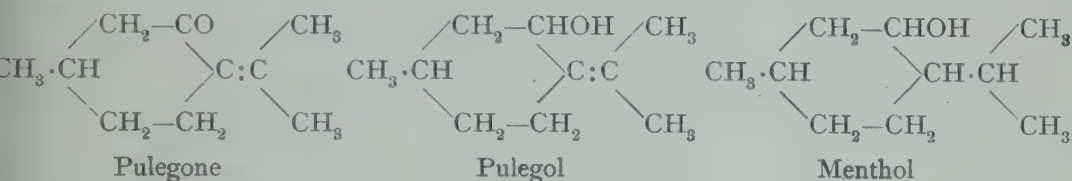
<sup>1)</sup> Berl. Berichte **39** (1906), 2577, 3960.

<sup>2)</sup> H. Hildebrandt, Zeitschr. f. physiol. Chemie **36** (1902).

<sup>3)</sup> Berl. Berichte **34** (1901), 2105.

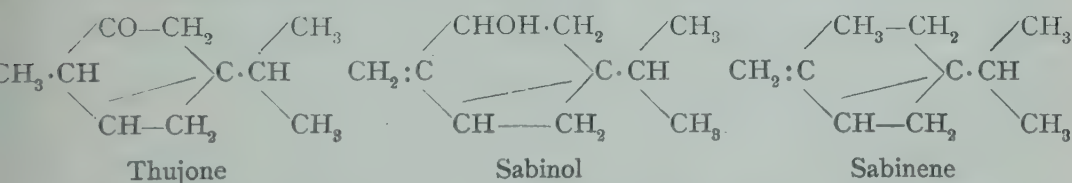
<sup>4)</sup> W. Lindemann, Arch. f. exp. Pharmakol. **42** (1899).

here the toxic action has diminished on the conversion in the alcohol-group, pulegol shows, according to Lindemann, the same action as pulegone. This may possibly be connected with the presence of the double linking in the lateral isopropyl chain; if this is removed by further reduction, we arrive at menthol, which is a but slightly active body, whereas the corresponding ketone menthone possesses at any rate a more powerful action.



In the relation between menthone and menthol, an analogous behaviour therefore shows itself as between camphor and borneol.

Closely related to thujone as to its structure is sabinol, which according to my examinations is the toxic principle<sup>1)</sup> of savin oil, in which it is present as acetate. It shows an action differing from that of all other camphor species, viz., an injurious action on the blood, which finds expression in this, that (in the dog) urine is passed which contains blood and also methæmoglobin. The toxic action corresponds to that observed in man, where savin oil, or decoctions of the branches, have been taken for the purpose of bringing about abortion. According to Semmler's<sup>2)</sup> examinations, sabinol is a hydroxyl derivative of the terpene sabinene in which an isopropyl and methylene group are situated in p-position; the latter is, according to Semmler, characteristic of the "pseudo-group" of the terpenes.



The terpene sabinene is a but slightly active body; in the organism, an oxidation takes place at one part of the ring, but apparently not at the same part where in sabinol the hydroxyl-group is situated; with this agrees the fact that, apart from the difference in toxicity, the products of conversion (or oxidation), obtained from the urine, are not the same.

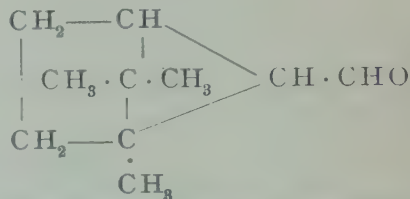
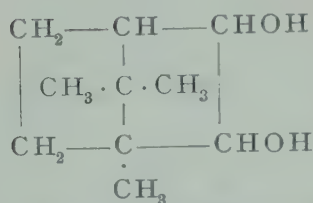
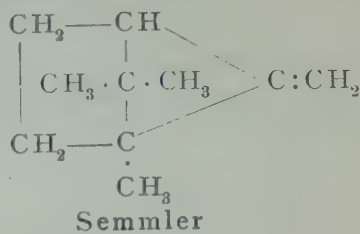
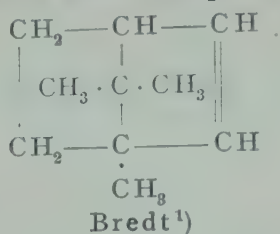
For camphene, which, according to Semmler's<sup>3)</sup> examinations, belongs to the pseudo-class of the terpenes, the conversions could be followed in the animal body, as it was found that camphene in the

<sup>1)</sup> H. Hildebrandt, Arch. f. exp. Pharmakol. **45** (1901).

<sup>2)</sup> Berl. Berichte **35** (1902), 2045.

<sup>3)</sup> Ibidem **33** (1900), 3423.

organism oxidises in the same manner as outside the body. The following formulæ have been accepted for camphene:—

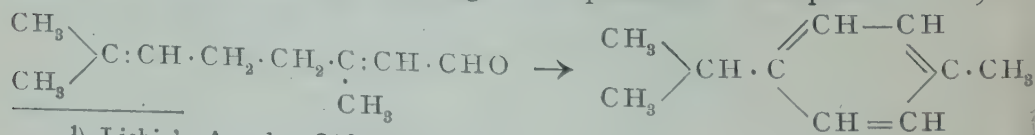


Camphene glycol (Wagner)<sup>2)</sup>

Camphenilane aldehyde (Bredt)<sup>3)</sup>

Wagner has obtained from camphene, by careful oxidation, camphene glycol, and has converted the latter by heating with dilute hydrochloric acid into an aldehyde, which Bredt considers identical with the camphenilane aldehyde produced by himself. In a similar manner the process in the organism may be imagined, inasmuch as in splitting up camphene glycol-glycuronic acid, this aldehyde is also formed, on the oxidation of which the acid  $\text{C}_{10}\text{H}_{16}\text{O}_2$  originates: isocamphenilic acid, m. p.  $118^\circ$ <sup>4)</sup>. According to this it is not improbable that other terpenes of the "pseudo" class experience an analogous change, from which, in the case of sabinene, the difference in the products of conversion as compared with those of sabinol can be explained. In the compounds belonging to the ortho-class of the terpenes, such as limonene, an oxidation of the methyl-group situated in p-position towards the isopropyl-group, into carboxyl, and also a hydroxylation in the nucleus, come under consideration.

Such an oxidation of a methyl-group situated on the ring has been detected with certainty in an aldehyde, viz., citral<sup>5)</sup> from lemongrass oil (although this aldehyde belongs to the aliphatic series). Citral also stands in close relation to p-cymene; Semmler<sup>6)</sup> converted it direct into p-cymene by heating with potassium bisulphate to  $190^\circ$ :



<sup>1)</sup> Liebig's Annalen **310** (1900), 134.

<sup>2)</sup> Berl. Berichte **23** (1890), 2309.

<sup>3)</sup> Liebig's Annalen **310** (1900), 116.

<sup>4)</sup> E. Fromm, H. Hildebrandt, P. Clemens, Zeitschr. f. physiol. Chemie **3** (1902); Report April **1903**, 81.

<sup>5)</sup> H. Hildebrandt, Arch. f. exp. Pharmakol. **45** and **46** (1901).

<sup>6)</sup> Berl. Berichte **24** (1891), 201.

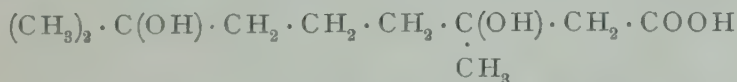
The ready conversion of the corresponding methyl-group of p-cymene into a carboxyl group has already been known for a long time: formation of cuminic acid<sup>1)</sup>. The dibasic acid formed after administering citral in the organism, has most probably the following constitution: —



i. e., 7-methyl octadiene-3,6-dicarboxylic-1,3 acid.

On the zinc dust distillation of the ammonium salt it yielded a pyrrol derivative which gave an intense colour reaction with pine-wood; for this reason, it belongs to the succinic acid series. When treated with sodium amalgam, the acid remained unchanged. Attempts of abstracting water by means of acetyl chloride were unsuccessful<sup>2)</sup>. Besides this crystalline acid, citral yields in the organism an isomeric amorphous acid<sup>3)</sup>, of which the product of inversion was obtained in crystalline form; it is probably formed by oxidation of one of the methyl-groups in the end-position. The dibasic acid is also formed in the organism after administration of geraniol, the alcohol corresponding to citral, whilst after giving nerol, only insignificant quantities can be detected in the urine. This shows either that nerol contains small quantities of geraniol, or that in the organism a partial conversion by displacement of a double linking takes place. Geranic acid<sup>4)</sup>, on the other hand, which is formed by oxidation of citral, yields abundant quantities of the dibasic acid after administering it to a rabbit.

Likewise as the aliphatic citral can be converted into two stereo-isomeric cyclic derivatives  $\alpha$ - and  $\beta$ -cyclocitral, geranic acid also can be converted into two corresponding cyclic products. Dilute acids act on aliphatic terpene compounds in such manner, that they dissolve the double linkings present by attaching the elements of water; the hydroxyl-groups then attach themselves preferably to the carbon atoms which carry methyl-groups<sup>5)</sup>. On hydrolysis of geranic acid there is formed first of all: —



The closing of the ring takes place in the first instance in the sense of formula I; according to the direction in which water is split off,  $\alpha$ - and  $\beta$ -cyclogeranic acids are formed: —

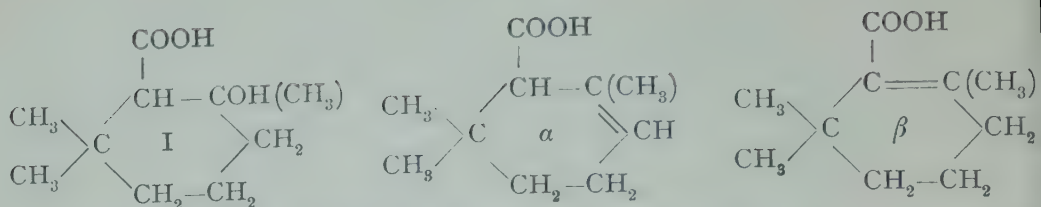
<sup>1)</sup> Ziegler, Arch. f. exper. Pharmakol. **1** (1873).

<sup>2)</sup> H. Hildebrandt and C. Harries, Beitr. zur Chemie u. Physiol. **4** (1903).

<sup>3)</sup> H. Hildebrandt, Arch. f. exper. Pharmakol. **46** (1901).

<sup>4)</sup> Berl. Berichte **26** (1893), 2717.

<sup>5)</sup> Tiemann, Berl. Berichte **28** (1895), 2137, and **31** (1898), 882.



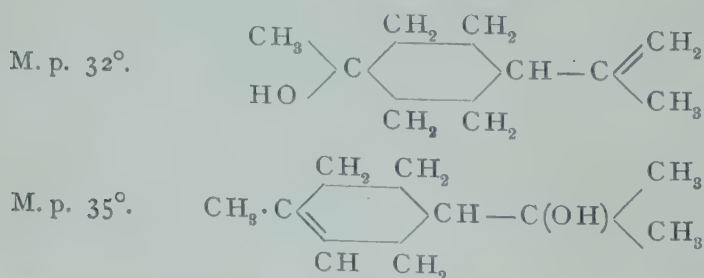
This behaviour explains that on the one hand the dibasic acid cannot be converted into the cyclic isomeride, and on the other, that in the cyclic isomerides an oxidation of the  $\text{CH}_3$ -group does not take place in the organism.

If the cyclic camphors cyclocitral and cyclogeraniol are compared from a physiological point of view with the aliphatic isomerides, it is conformably found that the latter have a more powerful action than the cyclic isomerides<sup>1)</sup>; a remarkable contrast therefore shows itself here to the behaviour of the previously discussed cyclic and aliphatic imines. But within these groups interesting differences also assert themselves, which are solely due to the difference in the position of the double bond.

Whilst geranic acid is still a fairly active body, the dibasic acid formed by oxidation of a methyl showed no action whatever even when 0,1 g. were injected into a frog.

Between  $\alpha$ - and  $\beta$ -cyclogeranic acids, important differences became apparent, inasmuch as  $\alpha$ -cyclogeranic acid acted like citral and geranic acid, though more feebly, whilst  $\beta$ -cyclogeranic acid was without any action whatever<sup>2)</sup>, even in a quantity of 0,3 g.

In what manner a difference in the position of the double bond influenced the action was proved by R. Matzel<sup>3)</sup>, who examined at my instigation the two isomeric terpeneols.



The combination-products with glycuronic acid isolated from the urine of the animals showed differences in the optical behaviour; the melting points of the free acids also were different.

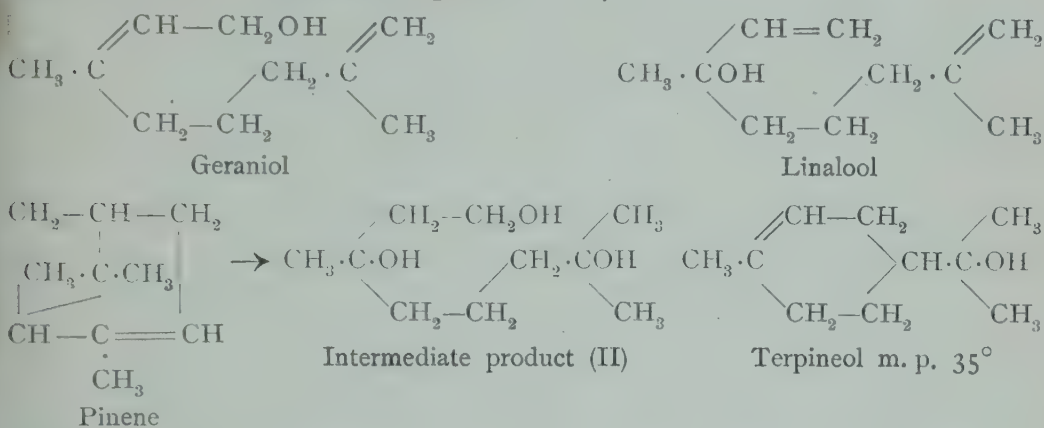
The two terpeneols can be converted by abstraction of water into the terpene limonene; the same may also indirectly be converted over

<sup>1)</sup> H. Hildebrandt, Arch. f. exp. Pharmakol. **46** (1901).

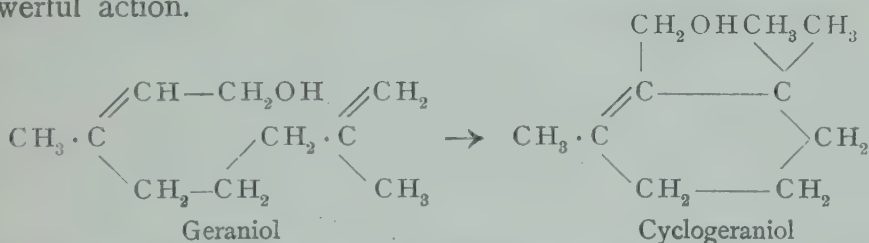
<sup>2)</sup> H. Hildebrandt, ibidem **46** (1901):

<sup>3)</sup> Arch. internat. de Pharmacodyn. **14** (1906). Comp. Report October 1905, 88.

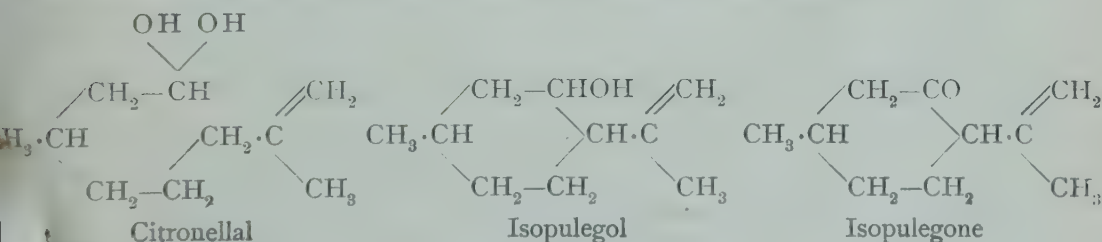
limonene monohalogenhydrate into terpineol ( $35^{\circ}$ ) (Semmler)<sup>1</sup>). The latter can be obtained directly from the aliphatic alcohols geraniol and linalool, and also from the terpene pinene, in the two last-named cases over the intermediate product II<sup>2</sup>):



Geraniol is converted by loss of water directly into limonene; L. Tschugaeff<sup>3</sup>) has also converted carvone into the latter; in carvone therefore the toxicity is solely due to the presence of the carbonyl-group. The more powerful action of the alcohols geraniol and linalool is due to their aliphatic structure; neither the terpineols nor cyclogeraniol<sup>4</sup>) (into which geraniol can be converted by ring-closure) show a powerful action.



From the aliphatic aldehyde citronellal we arrive by means of acetic acid anhydride at the alcohol isopulegol; by oxidation of the latter with chromic acid in glacial acetic acid, isopulegone  $\text{C}_{10}\text{H}_{16}\text{O}$  was obtained, which is very closely related to menthone.

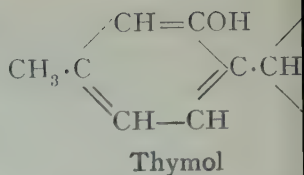
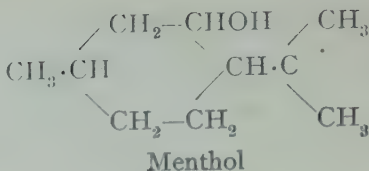
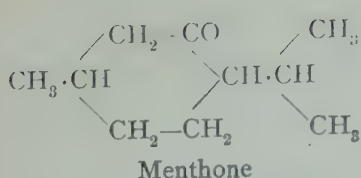


<sup>1</sup>) Berl. Berichte 28 (1895), 2190.

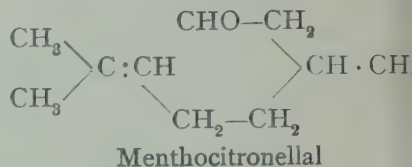
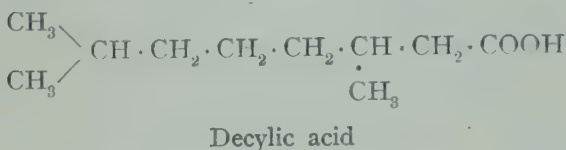
<sup>2</sup>) Semmler, Die ätherischen Öle, II., 339. Leipzig, 1906, Veit & Co.

<sup>3</sup>) Accord. to Chem. Zentralbl. 1905, I. 93.

<sup>4</sup>) H. Hildebrandt, Beitr. z. chem. Pathol. 4 (1904).



Recently Ciamician and Silber<sup>1)</sup> have converted menthone by exposure to light, into aliphatic decylic acid and into menthocytronellal.



The iso-compounds of pulegone and pulegol have not been examined with regard to their action; according to W. Lindemann<sup>2)</sup>, pulegone and pulegol are identical in their action. If the reduction of pulegone is carried still further, the C:C-group in pulegol is converted into CH·CH, and menthol is formed, which is much less toxic than pulegol. For this reason it is undoubtedly to the double bond in the side-chain that the toxic action of pulegone and pulegol is due.

The derivative designated by C. Harries and G. Roeder<sup>3)</sup> as  $\alpha$ -isopulegone is converted quantitatively, by prolonged standing in alcoholic solution with baryta water, into dextrorotatory pulegone. From this it would appear that a different behaviour of the iso-compounds with regard to the behaviour in the organism cannot be expected.

It is particularly interesting that the series of compounds here discussed stands in such close relation to thymol; menthol is a hexahydrated thymol. Thymol differs from the phenols by a specially feeble toxicity, and is known as a constituent of numerous essential oils. It does not appear impossible that in the plant itself conversion of phenols into the camphor-group also take place.

With regard to the bromatological experiments carried out by Zwaardemaker with muskone and other odoriferous substances, see under Musk, p. 107.

### Phyto-physiological Notes.

We have hitherto discussed under this heading the work dealing with the isolation of glucosides splitting off hydrocyanic acid, if at the same time benzaldehyde, or an allied body present in essential

<sup>1)</sup> Berl. Berichte **40** (1907), 2421; comp. the present Report p. 123.

<sup>2)</sup> Arch. f. exp. Pharmakol. **42** (1899).

<sup>3)</sup> Berl. Berichte **32** (1899), 3371.

oils, occurred. For this reason the work on plants yielding hydrocyanic acid in general, whose glucosides do not yield constituents of essential oils, does not come within the scope of our Reports, and we must therefore content ourselves with a bare reference to the following publications: Guignard<sup>1)</sup>, On the presence of a compound forming hydrocyanic acid in *Passifloræ*; Dunstan and Henry<sup>2)</sup>, On the formation of hydrocyanic acid in plants.

With regard to other glucosides yielding constituents of essential oils, see under Almond oil, bitter, p. 11.

During their chemical examinations of the vegetation of the odoriferous plants, Roure-Bertrand Fils<sup>3)</sup> have taken up the study of the relative solubility of the substances of which the individual organs in the various periods of the plant's life are composed. The experimental plant serving this purpose was *Ocimum basilicum* L. During the various stages of vegetation, the organs of the plant were separated and weighed; the material was then dried at 105° up to the constant weight, and next calcined. Further, 10 g. each of the dry substance were extracted with water to exhaustion in a Soxhlet apparatus, the aqueous extract was then evaporated to dryness, the residue thus obtained dried at 105°, and weighed. The number thus ascertained represented the "soluble substance"; on calcining the latter, the weight of the "ashes from the soluble substance" was found. From the difference, the weight of the organic substance could then be calculated. In the same manner the weight of the ashes and of the organic material in the insoluble substance were then ascertained, and finally all the figures obtained recalculated for 100 parts of the total dry substance.

The authors found that in the first stage of development of the plants, all organs have almost the same content of water; in the later stages the individual organs become poorer in water, and only the leaves retain approximately the same water-content.

Before the commencement of the blossoming period, the leaves contain in their dry substance most organic material. In the young plants these organs are less rich in soluble mineral matter than the stalk, but this is soon reversed. When the blossoming season commences, a decrease in the content of soluble organic substances and of total soluble material is observed in the dry substance of the roots, stalks, and leaves. The newly-forming inflorescences are at that time the part of the plant whose dry substance appears richest in soluble organic

<sup>1)</sup> Bull. des Sciences pharmacol. **13** (1906), 603.

<sup>2)</sup> Annal. de Chim. et Phys. **10** (1907), 118.

<sup>3)</sup> Bericht Roure-Bertrand Fils, April 1907, 6.

products, the opposite applying to the anorganic substances. The content of soluble organic matter in the leaf now soon begins to increase, and finally reaches an upper limit which is higher than in the other organs. Contrary to this, the content of organic substance in the inflorescences decreases very rapidly. It is remarkable that in the leaf the quantity of soluble substances does not fluctuate perceptibly, except at the period when the first inflorescences occur; about that time a large decrease takes place. With regard to the solubility of the anorganic substances the following facts were established: In the root, after an initial increase, a decrease of solubility is observed during the blossoming and also during the fructification, but in the end an increase occurs again. The solubility of the mineral substances present in the stalk diminishes up to the blossoming period, but increases again up to the end of the vegetation. In the leaves and inflorescences, the changes are imperceptible.

The authors established by comparative examinations of control plants growing up under normal conditions, and etiolised plants, that the latter are much richer in water than the former. The absence of light has this effect, that the dry substance shows a constantly increasing content of soluble products, not only of bodies of an anorganic, but also of those of an organic character.

In plants deprived systematically of their inflorescences, the weight of the system formed by the leaves and stalks is almost doubled. The cause of this may be looked for in the fact that the plant has been spared the loss of substance due to the work of fructification. The change in the solubility of the vegetable substance occurs in the same manner, both in the control plants and in those which have been systematically deprived of their inflorescences.

Two publications by E. Charabot and G. Laloue<sup>1)</sup>, on the formation and distribution of the essential oil, and on the migration of the odoriferous substances, in *Artemisia Absinthium* and *Verbena triphylla*, have already been discussed in our April Report<sup>2)</sup>.

### Hydrocarbons.

Pinene. The residual mixture of liquid chlorides obtained in producing pinene hydrochloride from American oil of turpentine has been examined by O. Aschan<sup>3)</sup>. By decomposing the chlorides with bases at increased temperature and by prolonged fractionating, finally over sodium, he obtained a terpene  $C_{10}H_{16}$  of the b. p. 145 to 148°.

<sup>1)</sup> Bull. Soc. chim. IV. 1 (1907), 280 and 640; Compt. rend. 144 (1907), 808; comp. Bericht Roure-Bertrand Fils, October 1906, 1.

<sup>2)</sup> Report April 1907, 126 and 127.

<sup>3)</sup> Berl. Berichte 40 (1907), 2250.

which he calls pinolene ( $d_{40}^{20} 0,8599$ ;  $[\alpha]_D + 1,63^\circ$ ;  $n_D 1,45768$ ; mol. refr. found 43,2, calculated for  $C_{10}H_{16}$  / 43,53). The molecular refraction shows that it is a bicyclic hydrocarbon with one double bond. By introducing hydrogen chloride into the ethereal solution of the terpene in the cold, a chloride  $C_{10}H_{17}Cl$  (m. p.  $38^\circ$ ;  $[\alpha]_D + 9,78^\circ$ ) was formed, which had a menthol- and camphor-like odour, and which readily splits off hydrochloric acid already when left standing in a closed vessel, or when brought in contact with water.

In chloroform solution pinolene absorbs one molecule bromine, but it does not yield a nitrosochloride, nor a nitrosite or nitrosate. It does not change when boiled with 20 per cent. oxalic acid solution or 10 per cent. sulphuric acid. By potassium permanganate solution it is attacked with somewhat greater difficulty than pinene, and there is then formed, besides other products, a syrupy acid which crystallises after some time (m. p. about  $200^\circ$ ). Treatment of pinolene with glacial acetic and sulphuric acids according to Bertram and Walbaum, led to the acetate of an alcohol  $C_{10}H_{17}OH$  (b. p.  $202$  to  $203^\circ$ ), which was oxidised to the ketone  $C_{10}H_{16}O$  (b. p. about  $200^\circ$ ). The semicarbazone of this ketone does not appear to be uniform, as it showed various melting points (about  $220^\circ$  and  $224$  to  $225^\circ$ ) according to the crude material employed, and the mother liquors contained another crystallising semicarbazone.

When equal quantities of pinolene hydrochloride and aniline were brought together, heat was spontaneously evolved, and aniline hydrochloride separated off. After working up the product, a hydrocarbon was obtained (b. p.  $154$  to  $155^\circ$  at 750 mm. pressure;  $d_{40}^{20} 0,8648$ ;  $[\alpha]_D + 5,46^\circ$ ,  $n_{D20,80} 1,47055$ ; mol. refr. found 43,77, calculated for  $C_{10}H_{16}$  / 43,53), which is neither identical with camphene nor with pinene, but which the author, on account of its resemblance to the latter, calls isopinene. It is also a bicyclic hydrocarbon with one double bond, and absorbs one molecule bromine and one molecule hydrochloric acid. The chloride  $C_{10}H_{17}Cl$  (m. p.  $36$  to  $37^\circ$ ;  $[\alpha]_{D220} + 9,18^\circ$ ) is as unstable as that of pinolene, and is also decomposed by aniline already in the cold, when it again yields back isopinene. Aschan reserves for the future a final decision on the identity of the two chlorides which would follow from this. Isopinene also yielded neither a nitrosochloride, nor a nitrosite. On treatment with glacial acetic and sulphuric acids according to Bertram and Walbaum, there is also formed an alcohol (b. p.  $202$  to  $203^\circ$ ) which can be oxidised into a ketone (b. p. about  $200^\circ$ , m. p. of the semicarbazone  $221^\circ$ ) with a menthol-like odour. When boiled with dilute sulphuric acid, isopinene is not split up, as well as pinolene. The author holds out a prospect of further information on the subject.

With regard to the synthesis of  $\beta$ -pinene from nopinone, see under Nopinone, p. 165.

**Camphene.** The melting point of natural camphene has frequently been found lower than that of the synthetic body. The question whether this occurrence must be attributed to impurities, or whether it is a case of another hydrocarbon, has induced Wallach<sup>1)</sup> to make a further examination of the natural camphene of Siberian pine needle oil. It was isolated in this manner, that the fraction of the saponified oil of the b. p. 156 to 165°, was oxidised with alkaline solution of potassium permanganate for the purpose of destroying the readily attacked portions, and the residue driven off with steam was strongly cooled. The camphene which had crystallised out was filtered off, and purified by distillation and fractional freezing out. It had the following properties: b. p. 160 to 161°; m. p. 39°;  $d_{40}^0$  0,8555;  $n_{D40}^0$  1,46207; molecular refr. found 43,71, calculated for  $C_{10}H_{16}$  43,53;  $[\alpha]_D - 84,9^\circ$  in 11,36 per cent. ethereal solution. On oxidising this camphene with potassium permanganate according to Wagner, a dibasic acid  $C_{10}H_{16}O_4$  (m. p. 142°;  $[\alpha]_D - 1,166^\circ$  in 20,85 per cent. alcoholic solution) isomeric with camphene-camphoric acid was formed, of which the chloride, the diamide (m. p. 197°) and the dianilide (m. p. 218°) were produced. It was clear from the melting points of these derivatives, that the acid obtained differs from the hitherto known camphene-camphoric acid. Besides the acid, there were formed in the oxidation, in small quantity, a glycol and an acid yielding a difficultly soluble sodium salt, two bodies the nature of which has not yet been cleared up. The natural camphene yielded isoborneol as readily as the artificial one. When treated with gaseous hydrochloric acid in ethereal solution, a chloride was formed, which was converted, by splitting off hydrogen chloride with aniline, into a camphene of the m. p. 51°. On brominating, a dibromide of the m. p. 89° was obtained. Wallach assumes that the natural camphene is a physical isomeride of the artificial camphene.

The camphene worked out from citronella oil yielded on oxidation the same acid melting at 142° as that of Siberian pine needle oil.

Wallach further produced, for comparison, artificial camphene from bornylamine, obtained by reduction of camphor oxime. The carefully purified base was converted in acetic solution with sodium nitrite, and the reaction-product was distilled with steam and fractionated. The camphene obtained (b. p. 160 to 161°; m. p. 50°;  $[\alpha]_D + 103,8^\circ$  in 9,67 per cent. ethereal solution), yielded on oxidation an acid of the m. p. 141 to 142°, whose mixture with the acid from natural

<sup>1)</sup> Nachr. K. Ges. Wiss. Göttingen 1907, Meeting of 20. July.

camphene showed a depression of the melting point. It has not yet been possible to carry out a further examination, owing to scarcity of material.

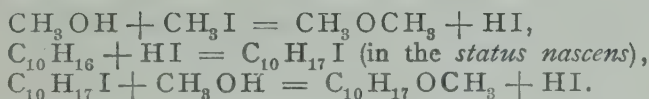
Reychler<sup>1)</sup> gives some information on the addition of methyl alcohol to camphene and trimethyl ethylene. If methyl alcohol (about 4 mol.) is heated with methyl iodide (1 mol.) for some hours in a tube to about 120 to 140°, methyl ether is formed according to the equation:



furthermore, methyl iodide is also formed back:



until the system has absorbed a definite quantity of water. This reaction, accomplished in the presence of l-camphene, yielded, besides gaseous methyl ether and a little unchanged terpene, chiefly inactive methyl isobornyl ether (b. p. 190 to 194°;  $d_{45}^{160}$  0,9235;  $n_{\text{yellow}, 160}$  1,46643; mol. refr. found 50,42, calculated 50,21). This shows that methyl alcohol has been attached to camphene under the catalysing influence of the hydrogen iodide, in accordance with the equations

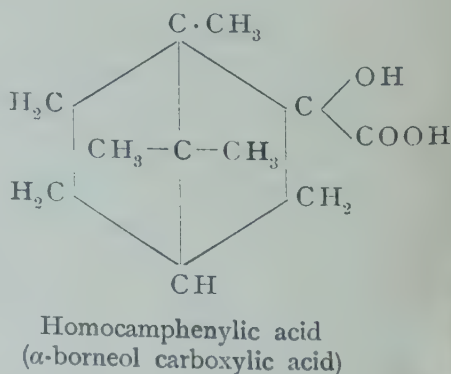
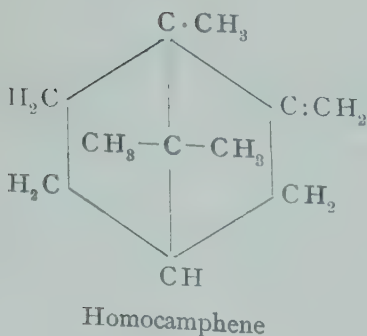
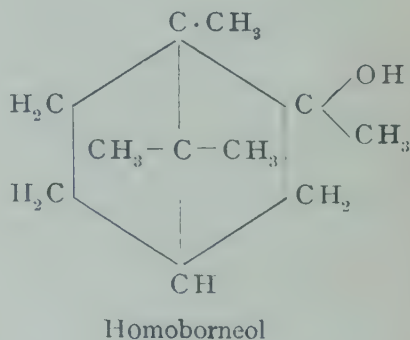
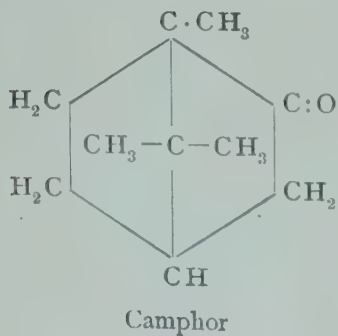


This catalytic action of small quantities of acid has already been known for a long time; for example, Bertram and Walbaum years ago employed dilute sulphuric acid in order to attach acetic acid to camphene, and Semmler as well as Hesse also knew the importance of this acid for the formation of ethers from camphene. In an analogous manner Reychler obtained from methyl alcohol, sulphuric acid, and trimethyl ethylene, at 95°, the corresponding methyl amyl ether (50% of the theoretical yield), in which case hydrogen methyl sulphate must be accepted as the catalyser. The addition or abstraction of water (in forming tertiary amyl alcohol or terpin hydrate, in splitting up pulegone, etc.), are reactions which must be attributed to the influence of the acid. Whether Bertram's reaction and its modifications are analogous to the hydration of trimethyl ethylene (conversion of a double into a single bond) or that of trimethylene (ring-opening with formation of n-propyl alcohol), cannot be determined in view of the present state of uncertainty as to the structure of camphene.

In the following pages, under fenchene, we refer to the formation of higher fenchene homologues according to Grignard's reaction. Accord-

<sup>1)</sup> Bull. Soc. chim. Belgique **21** (1907), 71; according to a copy kindly sent us.

ing to Wallach and Wienhaus<sup>1)</sup>, the analogous formation of higher homologues of camphene from camphor does not proceed equally well; anyhow, the action of methyl magnesium iodide on the latter in ethereal solution produced homoborneol, which was converted by loss of water into homocamphene (b. p. 166 to 168°, m. p. 28°). The principal object of this examination was the oxidation of the hydrocarbon with permanganate. There was then formed an acid  $C_{10}H_{16}(OH)COOH$ , which was identical with the acid obtained from crude fenchene containing camphor. This acid Wallach and Wienhaus designate as homocamphenylic acid, or better as  $\alpha$ -borneol carboxylic acid, which as a typical  $\alpha$ -hydroxy acid could be readily isolated in the form of its difficultly soluble sodium salt, and which was found to be isomeric with the  $\beta$ -hydroxycamphane carboxylic acid recently described by Bredt<sup>2)</sup>. When heated rapidly, the acid in question melted at 179°, but when heated very slowly already at 171°, probably owing to partial decomposition in the neighbourhood of the melting point;  $[\alpha]_D - 34,8^\circ$  in methyl alcohol),  $-30,72^\circ$  (in ether). When heated with dilute sulphuric acid and peroxide of lead, the acid was split up into camphor (m. p. 175°, dextrorotatory; semicarbazone m. p. 237°, lævorotatory) and carbonic acid.



<sup>1)</sup> Liebigs Annalen **353** (1907), 224.

<sup>2)</sup> Ibidem **348** (1906), 205; Report October 1906, 135.

Fenchene. The formation of isomeric fenchenes from fenchyl alcohol, which had been previously observed, induced Wallach<sup>1)</sup> to extend his examinations also to the higher homologues<sup>2)</sup> which can be produced with the help of Grignard's reaction from fenchone.

Homofenchyl alcohol ( $\alpha$ -methyl fenchol),  $C_{11}H_{19}OH$  had already been produced by Zelinski<sup>3)</sup> from d-fenchone and methyl magnesium iodide. But the product obtained by him, boiling at 208 to 209°, melting at 51 to 52° ( $[\alpha]_D + 11^\circ$  in alcoholic solution), could not be pure, for on continuing the fractionating, Wallach and Wienhaus obtained an alcohol whose melting point lay distinctly higher, whilst the optical activity was considerably lower. The purest portions of the homofenchyl alcohol produced by the last-named authors had the following properties: b. p. 215 to 216°; m. p. 61°;  $[\alpha]_D + 1,725^\circ$ ,  $+ 1,12^\circ$ ,  $+ 2,2^\circ$  (in ethereal solution). The solubility of the alcohol in all organic solvents is so high, that it cannot be recrystallised from any of them.

If homofenchyl alcohol is heated with  $2\frac{1}{2}$  times its quantity of fused and powdered potassium bisulphate for 1 to 2 hours in an oil bath to 160°, it is possible to distil over in a current of hydrogen a hydrocarbon solid at ordinary temperature, which after repeated distillation over sodium boils at 170 to 172°, but is not yet completely uniform, as it still contains small quantities of liquid portions (probably homocamphene). The body, homofenchene,  $C_{11}H_{18}$ , freed as much as possible from all impurities, melts at 32 to 37°, and has the following physical constants:  $d_{46 \text{ to } 47^\circ} 0,8520$ ;  $[\alpha]_D + 23,06^\circ$  (in ethereal solution);  $n_{D 46 \text{ to } 47^\circ} 1,4557$ . This hydrocarbon contains one ethylene linking. The oxidation of homofenchene with 4 per cent. permanganate solution takes place only very slowly; after repeating this operation several times, unattacked portions are obtained which can scarcely be considered as unsaturated, and consequently show the character of cyclene. The oxidation did not give unobjectionable results, as a fenchone had been used as crude material, whose camphor-content was not known at that time. The experiments shall be repeated with pure fenchone.

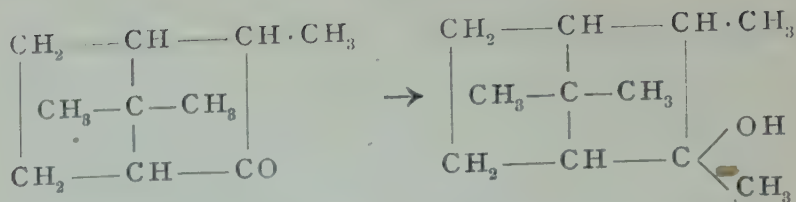
The progress of the reaction is shown by the following graphic formulæ (see page 142).

In accordance with the foregoing, the derivation of several hydrocarbons from homofenchyl alcohol can be imagined, which also would yield quite different products on oxidation.

<sup>1)</sup> Liebig's Annalen **315** (1901), 279; Report October 1901, 60.

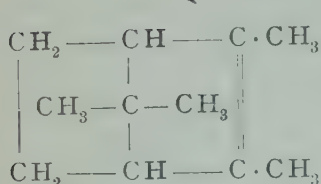
<sup>2)</sup> Ibidem **353** (1907), 218.

<sup>3)</sup> Ibidem **340** (1905), 17.

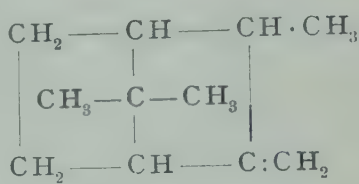


Fenchone

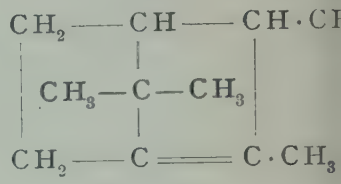
Homofenchyl alcohol



I.



II.



III.

Homofenchene

Terpinene. In our last Report (p. 137) we had occasion to mention the conversion of sabinene into terpinene compounds. In the meantime, our knowledge of the relation between the sabinene and the terpinene series has been enriched by a work of Wallach<sup>1)</sup>. In the same manner as nopinone (see p. 165) he also employed the sabina ketone  $\text{C}_9\text{H}_{14}\text{O}$

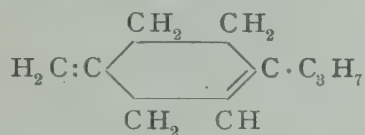


for syntheses which, as might be expected, led to terpinene derivatives,

By the action of methyl magnesium iodide on sabina ketone, Wallach obtained methyl sabinaketol, or sabinene hydrate  $\text{C}_{10}\text{H}_{18}\text{O}$ , which boils at 195 to 201° with slight loss of water, and melts at 38 to 39°. It has a terpineol-like odour, and is completely stable towards potassium permanganate. With glacial acetic acid and hydrogen bromide it yields, with dissolution of the tricyclic ring, terpinene hydrobromide; when shaken with 5 per cent. sulphuric acid, terpinene terpin (m. p. 137°) is formed. By the action of ethyl magnesium iodide, ethyl sabinaketol  $\text{C}_{11}\text{H}_{20}\text{O}$  was obtained from sabina ketone. The decomposition of the magnesium double compound was not in this case effected with an acid, but took place in a current of steam, as the alcohol, like the methyl compound, is sensitive towards acid. When shaken with dilute sulphuric acid it yielded the homologous terpinene terpin (m. p. 141 to 142°), which, when slowly heated, sublimes in white leaflets, and in contact with glacial acetic and hydrohalogen acids yields the corresponding halogen derivatives: dihydrochloride of the m. p. 67 to 68°, dihydrobromide of the m. p. 88 to 89°, dihydriodide of the m. p. 89 to 90°.

<sup>1)</sup> Nachr. K. Ges. Wiss. Göttingen 1907, Meeting of 20. July.

With the help of sabina ketone, Wallach was also able to carry out the synthesis of a terpinene ( $\beta$ -terpinene). The ketone was condensed in the usual manner with bromoacetic ester and zinc, into the hydroxy ester; from the latter, water was split off, the unsaturated ester formed was saponified, and the acid (m.p. 47 to 48°) slowly distilled at ordinary pressure. The hydrocarbon  $C_{10}H_{16}$  (b. p. 176°;  $d_0,843$ ;  $n_D,4773$ ; mol. refr. found 45,61, calculated for  $C_{10}H_{16}/2$  45,24) thus formed, with loss of carbonic acid, has two ethylene linkings, and behaves like terpinene. With glacial acetic acid and hydrogen chloride it yielded terpinene dihydrochloride (m.p. 52°), and with nitrous acid terpinene nitrosite, which could be identified by the nitrol-piperidide (m.p. 154°). To this terpinene, which he calls  $\beta$ -terpinene Wallach gives the following constitution:—



assuming that the intracyclic bond of sabina ketone is converted in the course of the reactions described into an ethylene bond, whilst the loss of water from the hydroxy ester, like in all analogous cases, takes place in the direction towards the side chain, so that in splitting off carbonic acid, a methene-group is formed. The formation of the ordinary terpinene nitrosite from the hydrocarbon would then be accompanied by a re-arrangement, — an assumption which requires further experimental support.

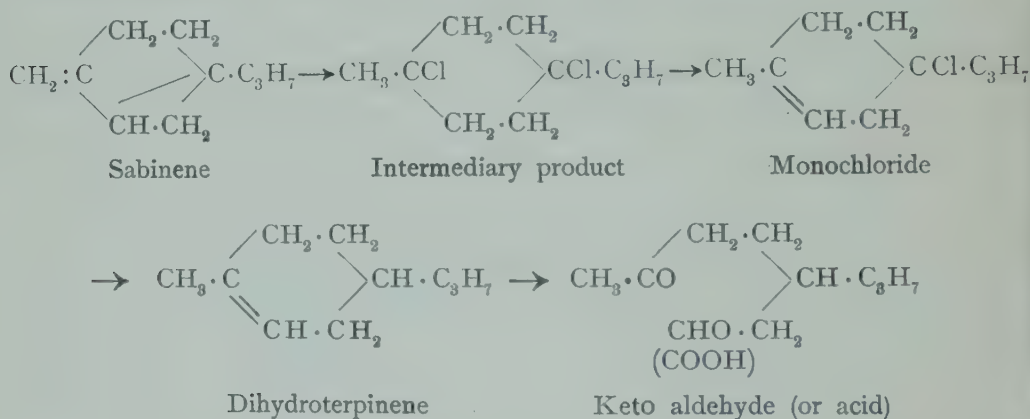
Sabinene. As mentioned by us in our last Report<sup>1)</sup>, Semmler obtained by treatment of sabinene with hydrochloric acid gas, a mixture of a mono- and a dihydrochloride. Wallach<sup>2)</sup> then showed that the monochloride alone is obtained, if every trace of moisture in the process referred to is excluded. Semmler<sup>3)</sup> has now also produced in this manner the monochloride, and has communicated the results of a detailed examination of the latter. By reducing the chloride (b.p. 82 to 86° at 9 mm. pressure;  $d_{20} 0,970$ ;  $n_D,482$ ;  $\alpha_D - 0^\circ 15'$ ) with sodium and absolute alcohol, there was obtained the hydrocarbon dihydroterpinene  $C_{10}H_{18}$  (b.p. 57 to 60° at 9 mm. pressure;  $d_{20} 0,8184$ ;  $\alpha_D + 12^\circ 30'$ ;  $n_D,4566$ ; mol. refr. found 45,4, calculated for  $C_{10}H_{18}/2$  45,64), which yielded a nitrosochloride (m.p. 87°) and a benzylnitrolamine (m.p. 107°). On oxidation with ozone, the keto aldehyde  $C_{10}H_{18}O_2$  (b.p. 119 to 125° at 9 mm. pressure;  $d_{20} 0,9439$ ;

<sup>1)</sup> Report April 1907, 140.

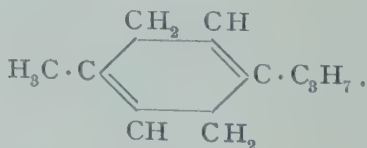
<sup>2)</sup> Ibidem, 141.

<sup>3)</sup> Berl. Berichte 40 (1907), 2959.

$n_D$  1,44962; disemicarbazone, m. p.  $183^\circ$ ) was formed; with potassium permanganate, a methyl keto acid  $C_{10}H_{18}O_3$  (b. p.  $174$  to  $180^\circ$  at 9 mm. pressure;  $d_{20}^{20}$  1,019;  $n_D$  1,45662; mol. refr. found 49,62, calculated for  $C_{10}H_{18}O_3$  50,02). This shows that the dihydroterpinene is identical with carvomenthene which Semmler<sup>1)</sup> had previously obtained by the reduction of limonene monohydrochloride and of phellandrene. In the author's opinion, a re-arrangement must for this reason take place in the production of the monohydrochloride from sabinene, inasmuch as intermediately a dichloride is formed, from which HCl is immediately split off, as is expressed in the following formulæ: —



As the monochloride can readily be converted into the dichloride, and the latter further into terpinene<sup>2)</sup>, Semmler follows up the description of the above-named experiments with a theoretical contemplation regarding the formula of terpinene, in which he arrives at the result that the following constitution must be ascribed to this hydrocarbon: —



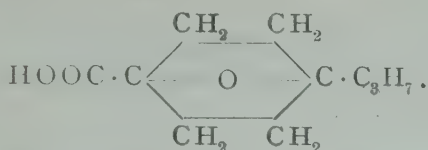
Similar to the formation of the monochloride from sabinene, he also imagines the conversion of camphene into isobornylchloride, and of pinene into bornylchloride. One molecule HCl attaches itself to the bridge-bond, with ring-disruption, whilst a second molecule HCl becomes attached to the double-bond, and immediately becomes liberated again, with formation of a new double-bond (or new ring).

On oxidising sabinene with potassium permanganate, Semmler obtained, in addition to the previously described  $\alpha$ -hydroxy acid, an

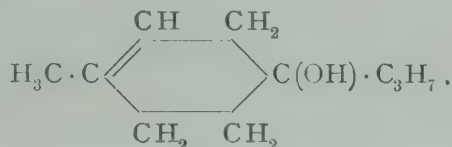
<sup>1)</sup> Berl. Berichte **36** (1903), 1035 and 1753; Report October 1903, 83.

<sup>2)</sup> Ibidem **40** (1907), 588; Report April 1907, 141.

oxide acid  $C_{10}H_{16}O_3$  (b. p.  $140^\circ$  at 9 mm. pressure), for which he proposes the following formula:—



A short time ago Semmler<sup>1)</sup> obtained from sabinene and concentrated formic acid an alcohol  $C_{10}H_{18}O$ , which was identical with the alcohol  $C_{10}H_{18}O$  of oil of sweet marjoram ("terpinenol" Wallach, "origanol" Semmler). The formula drawn up at the time is now corrected by Semmler to the following:—



which confirms the formula accepted by Wallach<sup>2)</sup> for this alcohol.

With regard to the conversion of sabinene into terpinene compounds, see under Terpinene (p. 143).

**Sylvestrene.** The process of substituting hydroxyl for chlorine employed by Wallach<sup>3)</sup> in the case of terpinene dihydrochloride, to which we referred in our last Report, has recently also been applied by this investigator<sup>4)</sup> to sylvestrene dihydrochloride  $C_{10}H_{16} \cdot 2 \text{HCl}$ . 10 g. chloride (m. p.  $72^\circ$ ) were shaken with a hot solution of 10 g. caustic potash in 500 cc. water, and the product after 5 hours distilled with steam. The residue contained sylveterpin  $C_{10}H_{18}(\text{OH})_2$  (m. p.  $135$  to  $136^\circ$ ;  $[\alpha]_D + 27.43^\circ$  in methyl-alcoholic solution), and the distillate, besides some hydrocarbon, sylveterpineol  $C_{10}H_{17}\text{OH}$  (b. p.  $210$  to  $214^\circ$ ;  $d_{20} 0.924$ ;  $n_{D20} 1.4822$ ; mol. refr. found 47.53, calculated for  $C_{10}H_{17} \cdot \text{OH} = 47.96$ ), which on shaking with concentrated hydrochloric acid, yielded back sylvestrene dihydrochloride. On oxidation of sylveterpineol with 1 per cent. solution of potassium permanganate in the cold, the corresponding glycerol  $C_{10}H_{17}(\text{OH})_3$  of the b.p.  $165^\circ$  (11 mm. pressure) was formed; this is an almost colourless, viscid oil, which did not crystallise.

The nitrosochloride of sylvestrene passed over, in splitting off hydrogen chloride, into an oxime, which could not be obtained in solid form, but which on boiling with oxalic acid yielded a ketone, whose semicarbazone (m. p.  $175$  to  $177^\circ$ ) pointed to the composition

<sup>1)</sup> Berl. Berichte **39** (1906), 4421; Report April 1907, 141.

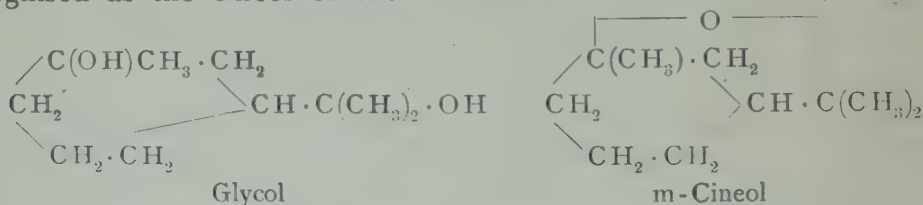
<sup>2)</sup> Ibidem **40** (1907), 596; Report April 1907, 137.

<sup>3)</sup> Liebig's Annalen **350** (1906), 153; Report April 1907, 135.

<sup>4)</sup> Nachr. K. Ges. Wiss. Göttingen 1907, Meeting of 8. June.

$C_{10}H_{14}O$ . A more detailed examination could not be carried out, owing to lack of material.

**Carvestrene.** The synthesis of carvestrene discussed by us in our Report of April 1907, 145 after a preliminary communication, has since then been described in detail by the authors Perkin jun. and Tattersall<sup>1)</sup>. To complete the information given by us we have still to mention a series of experiments on the lines of the heretofore-mentioned reaction of p-cyclohexanone carboxylic ester with  $CH_3MgI$ . It was proved that the action of methyl magnesium iodide on m-cyclohexanone carboxylic ester forms, besides m-methyl-m-cyclohexanolic acid, a not unimportant quantity of a neutral oil which consists for about one half of dihydrocarvestrenol or  $\Delta_1$ -m-menthenol-8; there also occurs a crystalline substance melting at  $127^\circ$ , which was found to be trans-tetrahydrocarvestrenediol, identical with the corresponding glycol obtained from trans-carvestrene dihydrobromide, through the diacetate; and finally an oil distilling at  $177$  to  $178^\circ$ , which was recognised as the cineol of the m-series: —



The m-cineol which is probably formed from the glycol by the water-abstracting action of the  $CH_3MgI$ , has a pungent camphor-like odour, and shows in its properties a certain resemblance to ordinary cineol; with hydrogen bromide it yields, in a manner analogous to the latter, a mixture of much cis- and little trans-carvestrene dihydrobromide.

**Myrcene, ocimene.** The *Receuil des travaux chimiques des Pays-Bas*<sup>2)</sup> contains a first communication by Enklaar on the aliphatic terpenes and their derivatives, the principal contents of which have already been communicated by us after the author's thesis<sup>3)</sup>. We would still add here the constants of allo-ocimene which Enklaar has examined more in detail, and which according to van Romburgh is formed by a re-arrangement from ocimene when the latter is heated. This geometric isomeride of ocimene boils at  $188^\circ$  (750 mm. pressure), i. e.,  $16^\circ$  higher than the original terpene; at 12 and 24 mm. pressure, its boiling point is  $81$  and  $95^\circ$  respectively. The further constants are:  $d_{16^\circ} 0,8172$ ;  $d_{15^\circ} 0,8182$ ;  $n_{D16^\circ} 1,5296$ . The chemical properties of allo-ocimene have already been reported upon by us.

<sup>1)</sup> Journ. Chem. Soc. 91 (1907), 480.

<sup>2)</sup> Receuil des trav. chim. des P.-B. 26 (1907), 157.

<sup>3)</sup> Report April 1906, 109.

## Alcohols.

Borneol. The isomerisations occurring when phosphorus or hydrogen halogenides act on secondary hydroaromatic alcohols or glycols, have been explained by Kondakow and his collaborators in earlier works thus, that during the first phase of the reaction a complete or partial racemisation and geometric isomerisation takes place. There are further formed independent haloid derivatives of different stability, which probably depends upon the stereochemical position of the halogen and the hydrogen atoms. The unstable isomerides among these secondary ones are readily converted into tertiary haloid anhydrides, and that either on account of an atomic migration, or by the abstraction of the hydrohalogen, and its reattachment at another place. In some hydroaromatic alcohols a rearrangement of the carbon nucleus may then take place. But with regard to the behaviour of the alcohols, their esters and ethers, towards the hydrohalogen acids, with reference to the formation of isomerides, nothing is as yet known. Kondakow and Schindelmeiser<sup>1)</sup> examined in this respect the behaviour of the l-bornylacetate of the m. p.  $29^{\circ}$  and the rotatory power  $[\alpha]_{D18^{\circ}} - 43,63^{\circ}$ , frozen out from the oil of *Abies sibirica*, which yielded on saponification a l-borneol of the m. p.  $203$  to  $204^{\circ}$  and the rotation  $[\alpha]_{D20^{\circ}} - 30,16^{\circ}$ . When treated with glacial acetic and hydrochloric acids (for 3 hours at  $125^{\circ}$ ), a pure pinene hydrochloride of the m. p.  $124^{\circ}$  was formed. After recrystallisation from alcohol, it was stable towards alcoholic solution of silver nitrate; heating with water to  $120^{\circ}$  only split off 25% of the (total?) chlorine. After this treatment the hydrochloride showed the melting point  $118$  to  $121^{\circ}$ , possibly due to the presence of camphene. In every case the hydrochloride was inactive. A fresh proof had therefore been given of the identity of bornyl chloride with pinene hydrochloride. The authors summarise in tabulated form the rotatory values of pinene (d- and l-) and the corresponding halogenhydrates, as ascertained by previous investigators. In the same manner they treated a fenchyl acetate obtained from l-fenchyl alcohol of the m. p. above  $45^{\circ}$  and the rotation  $[\alpha]_D - 15^{\circ} 22'$ , by heating with acetic anhydride to  $155$  to  $160^{\circ}$ . The acetate, whose constants were as follows:  $d_{20^{\circ}} 0,972$ ;  $[\alpha]_D - 63^{\circ} 24'$ ;  $n_D 1,4565$ ; b. p.  $91$  to  $91,5^{\circ}$  (12 mm. pressure) or  $[\alpha]_D - 61^{\circ} 10'$  and b. p. as above respectively, when heated with glacial acetic and hydrochloric acids to  $100^{\circ}$ , was not completely converted into the chloride; the product had  $d_{20^{\circ}} 0,952$ ;  $n_D 1,4758$ ;  $[\alpha]_D 0$ ; b. p.  $68$  to  $74^{\circ}$  (11 mm. pressure), and reacted with silver nitrate. When this chloride was treated with alcoholic potash, little inactive fenchene of the b. p.  $145$  to  $166^{\circ}$  was formed; the bulk remained unchanged, but probably owing to admixtures (possibly fenchyl

<sup>1)</sup> Journ. f. prakt. Chem. II. 75 (1907), 529.

alcohols, fenchone, fenchene polymerides) it could not be converted into the solid inactive chloride boiling at  $76$  to  $78^{\circ}$   $12$  (mm. pressure) which is stable towards silver nitrate.

The experiments made by the authors showed that hydrochloric acid has practically the same action on both acetates. The slight deviations observed in fenchyl acetate are explained by the assumption of a greater tendency to isomerisation.

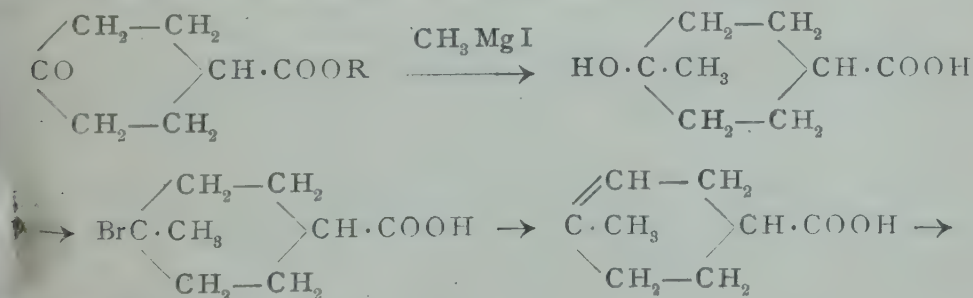
Kondakow<sup>1)</sup> has also examined some derivatives of isofenchyl alcohol. This alcohol, the member of the fenchane series which has hitherto been examined least of all, is, according to some investigators, a mixture of chemically identical, but optically differing, alcohols; according to others, it is a mixture of tertiary, or of tertiary and secondary alcohols; or a stereomeric fenchyl alcohol; or finally a mixture of a liquid fenchyl-alcohol and a solid stereomeric isofenchyl alcohol. The reactions known up to the present do not admit of a decision either one way or the other.

Kondakow produced from several fenchenes of different rotatory power, according to his zinc chloride method, the acetic ester of isofenchyl alcohol. The resulting alcohol was a mixture of a solid body (m. p.  $61,5$  to  $62^{\circ}$ ,  $[\alpha]_D - 25,73^{\circ}$ ) and a liquid isomeride ( $d_{15^{\circ}} 0,963$ ;  $n_D 1,48008$ ;  $\alpha_D - 13^{\circ} 44'$ ; b. p.  $88$  to  $88,5$  [ $10$  mm. pressure] and  $97$  to  $98^{\circ}$  [ $13$  mm. pressure] respectively). The acetates were partly dextrorotatory ( $[\alpha]_D + 5^{\circ} 33'$ ), partly lævorotatory ( $[\alpha]_D$  up to  $-9^{\circ} 35'$ ), and partly inactive, and had approximately the same constants:  $d_{\frac{20^{\circ}}{4^{\circ}}} 0,9752$  to  $0,9784$ ;  $n_D 1,46168$  to  $1,46257$ ; molecular refraction  $48,34$  (inactive acetate) to  $55,07$  (d-acetate); b. p.  $95$  to  $97^{\circ}$  (i-acetate);  $90$  to  $100^{\circ}$  and  $100$  to  $105^{\circ}$  (l- and d-acetates respectively;  $15$  mm. pressure). From the l- and the i-acetates, lævorotatory alcohols were obtained which contained in their first fractions inactive portions remaining liquid; the subsequent portions were solid (m. p.  $48$  to  $53^{\circ}$ ,  $54$  to  $55^{\circ}$ ), and lævorotatory. In the various hydrations there always remained behind a portion of the fenchene amounting to about  $10\%$  of the quantity worked up, whose rotation, boiling point, and specific gravity were lower than those of the original material. The experiments showed that there exist on the whole no definite relations between the acetates and the corresponding alcohols, except that the acetates had approximately the same, and the isofenchyl alcohols different rotations. Optically inactive isofenchyl alcohol of the b. p.  $80$  to  $81^{\circ}$  (pressure not mentioned) yielded, on treatment with phosphorus pentachloride, a chloride of the b. p. (of the bulk)  $73$  to  $74^{\circ}$  ( $9$  mm. pressure);  $d_{20^{\circ}} 0,996$ ;  $n_D 1,4812$ ;  $[\alpha]_D - 3^{\circ} 53'$ ; molecular refraction

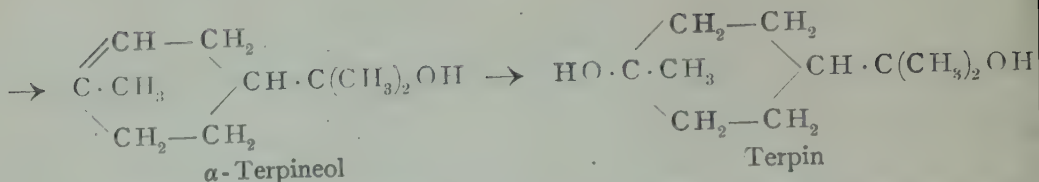
<sup>1)</sup> Journ. f. prakt. Chem. II. 75 (1907), 539.

49,02. This chloride did not split off hydrochloric acid on standing, but when treated with silver nitrate in alcoholic solution it yielded almost the whole of the chlorine; with alcoholic potash, it regenerated, in addition to very little fenchene, the liquid alcohol. After standing for 24 hours with water it formed, however, a solid dextrorotatory alcohol melting between  $61,5$  and  $65^{\circ}$ , which was already formed from a part of the chloride on washing the latter for the purpose of freeing it from phosphorus oxychloride. These experiments are intended to prove that on conversion of the alcohol into the hydrochloride, an optical isomerisation takes place; from the liquid isofenchyl alcohol there is formed, through the chloride, the solid isofenchyl alcohol melting at about  $65^{\circ}$ , the same as previously from fenchene by the old method over fenchene hydrochloride. This shows that isofenchyl chloride and fenchene hydrochloride are structurally identical. The mutual relationship of the two alcohols is explained by Kondakow thus, that the liquid alcohol is a racemic one, or represents a mixture of stereomerides, of which the dextrorotatory is unstable; or, finally, the liquid alcohol contains a tertiary alcohol which is readily converted with phosphorus pentachloride into solid secondary isofenchyl alcohol. The relationship of the solid isofenchyl alcohol towards fenchyl alcohol is not yet cleared up. Both yield on oxidation ketones, fenchone and isofenchone, with almost identical physical constants, but with derivatives of different melting points; they also yield on reduction different alcohols; fenchone yields quantitatively isofenchyl alcohol, isofenchone a liquid alcohol of the b. p.  $83$  to  $84^{\circ}$  (9 mm. pressure) which has already been described by Bertram and Helle. Kondakow further explains in detail the probable reaction-mechanism during the formation of this alcohol, which Semmler had previously discussed, and he comes to the conclusion that it is probably a case of a tertiary alcohol which corresponds to a new fenchone.

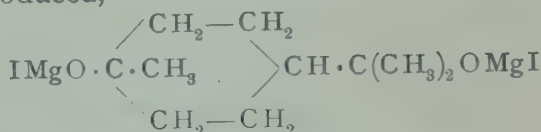
Terpin. At the commencement of their experiments with regard to terpene syntheses, Kay and Perkin jun.<sup>1)</sup> had converted p-cyclohexanone carboxylic ester, by treatment with methyl magnesium iodide, etc., in the usual manner, into  $\alpha$ -terpineol and terpin: —



<sup>1)</sup> Journ. chem. Soc. 85 (1904). 658.



It was remarkable that at the time, in the first conversion with  $\text{CH}_3\text{MgI}$ , only a comparatively small yield was obtained. Recent experiments by the same authors<sup>1)</sup> now show clearly that the bad yield is due to the fact that, besides the  $\text{CO}$ -group, also simultaneously the carboxethyl-group enters into action with Grignard's reagent; from the body thus produced,



there is also easily formed cis-terpinhydrate of the m. p.  $107^\circ$ . The synthesis of this product, which was obtained in a quantity of at most 7 g. from 50 g. ketonic acid ester, is therefore greatly simplified by this secondary reaction.

Linalool. Roure Bertrand Fils<sup>2)</sup> believe that the question, whether linalool is really a tertiary alcohol or not, has been finally solved by them by a comparative study of the esterification of linalool and geraniol. The two alcohols were submitted to esterification with glacial acetic acid, for which 6 mol. acetic acid were used to 1 mol. of the two carbinols. The mixtures were left standing in a room which was but little subject to fluctuations of temperature. The progress of the esterification was ascertained by determining the ester-content of several samples.

After 24 hours there were formed, in parallel tests, 5,5 % geranyl acetate but only 0,4 % linalyl acetate;

after 10 days, 29,2 % geranyl acetate, but only 0,6 % linalyl acetate.

" 24 " 45,0 % " " " " 1,1 % " "

" 5 months, 85,6 % " " " " 3,9 % " "

" 12 " 90,0 % " " " " 5,3 % " "

For geraniol this result corresponds to that which might be expected in the case of a primary alcohol; the extremely slow progress of the esterification in linalool, however, appears to be only possible with a tertiary alcohol.

With regard to the determination of hydroxyl groups according to Zerewitinoff, and of linalool according to Boulez, see under Analytical Notes, p. 117 and 119.

<sup>1)</sup> Journ. chem. Soc. 91 (1907), 372.

<sup>2)</sup> Bericht Roure-Bertrand Fils, April 1907, 1.

## Oxides.

Cineol. Compounds of cineol with anorganic and Grignard's salts, have been produced by R. H. Pickard and J. Kenyon<sup>1</sup>). According to the authors' researches, the two addition products of cineol with  $\alpha$ - and  $\beta$ -naphthol of the m. p.  $78^\circ$  and  $50^\circ$  respectively, consist of molecular quantities of the corresponding components. Cineol hydrogen cobalticyanide, already described previously by v. Baeyer and Villiger, contains for 3 mol. cineol, 1 mol.  $\text{H}_3\text{Co}(\text{CN})_6$ . Cineol zinc iodide  $(\text{C}_{10}\text{H}_{18}\text{O})_2 \cdot \text{ZnI}_2$  is obtained in the form of colourless needles of the m. p.  $130$  to  $131^\circ$ , from an alcoholic solution of zinc iodide containing cineol. The compound is decomposed by boiling with water. Cineol cadmium iodide has a composition analogous to the foregoing compound; it melts indistinctly. Cineolic acid forms with hydrogen cobalticyanide an addition product of the formula  $(\text{C}_{10}\text{H}_{16}\text{O}_5)_3 \cdot \text{H}_3\text{Co}(\text{CN})_6$ , which does not yet melt at  $285^\circ$ . With ethyl magnesium iodide in a dry ether solution, cineol yields a yellowish, very hygroscopic precipitate of the formula  $(\text{C}_{10}\text{H}_{18}\text{O})_2 \cdot \text{C}_2\text{H}_5\text{MgI}$ . But if an excess of Grignard's salt is added to cineol, there results a viscid oil, which is converted in a hard mass, with evolution of gas (probably ethane), when heated to  $170$  to  $190^\circ$ . If it is heated rapidly the product decomposes in an explosive manner with separation of iodine, and formation of p-cymene and polymerised compounds. When treated at  $0^\circ$  with dilute sulphuric acid, the addition-product is converted into an oil from which the authors isolated by distillation with steam, terpineol of the m. p.  $35^\circ$  and b. p.  $107^\circ$  (18 mm. pressure) ( $\Delta_1$ -p-menthenol-8). The terpineol was identified by the usual derivatives (nitrosochloride of the m. p.  $120^\circ$ , phenyl urethane of the m. p.  $110^\circ$ , etc.). From the portion of the oil not volatile with steam, a diterpene  $\text{C}_{20}\text{H}_{32}$  of the b. p.  $191^\circ$  (18 mm. pressure) was isolated. Terpineol was also obtained when using methyl magnesium iodide or ethyl magnesium bromide.

With regard tho the m-cineol of Perkin jun. and Tattersall, see under Carvestrene, p. 146.

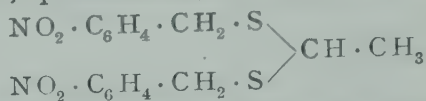
## Aldehydes.

As a qualitative reagent on aldehydes and ketones, A. Schaeffer and A. Murúa<sup>2</sup>) recommend p-nitrobenzyl mercaptan, which differs favourably from other mercaptans by its crystallisation-capability, its feeble odour, and the tendency to yield readily crystallising mercaptals or mercaptols respectively. According to the directions of Pfyl and

<sup>1</sup>) Journ. chem. Soc. **91** (1907), 897.

<sup>2</sup>) Berl. Berichte **40** (1907), 2007.

Waters<sup>1)</sup>, these bodies are produced by dissolving p-nitrobenzyl zinc mercaptide in alcohol saturated with hydrochloric acid, and mixing it with the calculated quantity of the aldehyde in question. The separation mostly occurs at once, rarely only after 24 hours' standing in the cold. The authors produced first of all the following bodies: —  
From acetic aldehyde, p-nitrobenzyl ethylidene mercaptal, m. p. 82°:



- „ salicylic aldehyde, p-nitrobenzyl o-hydroxybenzylidene mercaptal, m. p. 152°.
- „ cinnamic aldehyde, p-nitrobenzyl phenylpropenylidene mercaptal, m. p. 140°.
- „ cuminol, p-nitrobenzyl p-isopropyl benzylidene mercaptal, m. p. 84°.
- „ menthone, menthone p-nitrobenzyl mercaptol, m. p. 171°.
- „ pulegone, pulegone p-nitrobenzyl mercaptol, m. p. 133°.
- „ furfural, p-nitrobenzyl furfurylidene mercaptal, m. p. 87°.

With regard to the determination of aldehydes and ketones according to Rother and

With reference to the hæmatospectroscopic method of Bruylants for the identification and determination of aldehydes, see under Analytical Notes, pp. 120 and 122.

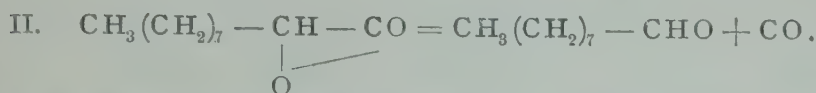
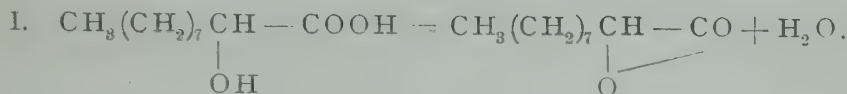
Nonylic aldehyde. Of the normal fatty aldehydes, nonylic aldehyde and decylic aldehyde are particularly important as constituents of essential oils. According to P. Bagard<sup>2)</sup>, the former can be obtained by dry distillation of  $\alpha$ -hydroxy capric acid, the latter by distillation of  $\alpha$ -hydroxy undecylic acid. Starting from pelargonic acid, Bagard produced hydroxy capric acid by first of all reducing pelargonic acid according to Bouveault and Blanc<sup>3)</sup>, by treating its ethyl ester with sodium, into nonylic alcohol. Through the nonyl bromide and nonyl cyanide obtained from nonylic alcohol, he arrived at capric acid, which was then converted by brominating into  $\alpha$ -bromocapric acid. The latter acid, when boiled with potassium carbonate solution, yielded  $\alpha$ -hydroxy capric acid. In order to obtain  $\alpha$ -hydroxy undecylic acid, he used as crude material undecylenic acid, which was first of all converted into undecylic acid by addition of hydrogen iodide and subsequent reduction with zinc. By brominating the undecylic acid, and replacing the bromine with the hydroxyl-group as above,  $\alpha$ -hydroxy undecylic acid was formed. The yield of nonylic aldehyde was 71%, that of decylic aldehyde 52%, of the hydroxy acids.

<sup>1)</sup> Thesis, Munich, 1905.

<sup>2)</sup> Bull. Soc. Chim. IV. 1 (1907), 346.

<sup>3)</sup> Compt. rend. 136 (1903), 1676.

The reaction proceeds in two phases. There is first of all formed, with abstraction of water, a lactide, which on further heating splits up into CO and aldehyde.



Of the two aldehydes, various derivatives suitable for identification were produced. The oxime of decylic aldehyde melts at  $69^\circ$ ; the semicarbazone of nonylic aldehyde at  $100^\circ$ . The latter statement leads Harries and Türk<sup>1)</sup> to a rectification of their previous communications. They had found for the melting point of the semicarbazone of nonylic aldehyde  $84^\circ$ <sup>2)</sup>. But a subsequent check test showed that this compound melts at  $100^\circ$ , in agreement with Bagard's observation, if it is produced from the aldehyde purified by the bisulphite compound.

**Protocatechuic aldehyde.** Among the derivatives of pyrocatechol, protocatechuic aldehyde, valuable for syntheses on account of its aldehyde-group, and also employed for the production of vanillin, possesses in a special degree properties which do not render it particularly inviting for working up. H. Pauly<sup>3)</sup> endeavoured to convert piperonal directly into the cyclic carbonate, thus avoiding protocatechuic aldehyde, i. e., to change in the piperonal the group  $:\text{O}_2\text{CH}_2$  into  $:\text{O}_2\text{CO}$ . Finally he succeeded to replace in dichloropiperonal<sup>4)</sup> obtained from piperonal, the two chlorine atoms by oxygen and so to produce the cyclic carbonic acid ester. Fittig and Remsen were unable, in the attempt made by them of decomposing the dichloropiperonal, to isolate the carbonate, as it is spontaneously decomposed further by boiling water. This can only be successfully accomplished if water is allowed to act in masked form, or indirectly, on the dichloride. For this purpose anhydrous oxalic acid for example is very suitable; at about  $130^\circ$  it reacts with dichloropiperonal according to the following equation:—



Concentrated sulphuric acid can also be employed in combination with water for the conversion of the group  $:\text{O}_2\text{CCl}_2$  into  $:\text{O}_2\text{CO}$ ;

<sup>1)</sup> Berl. Berichte **40** (1907), 2756.

<sup>2)</sup> Ibidem **39** (1906), 3733.

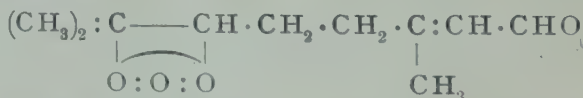
<sup>3)</sup> Ibidem **40** (1907), 3096; German Patent application P. 18466, Class 120.

<sup>4)</sup> Liebig's Annalen **159** (1871), 126.

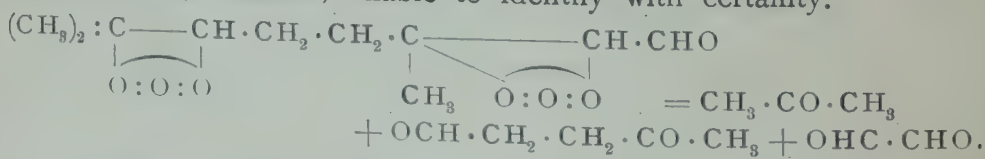
here the reaction in the cold proceeds easily, and the total chlorine escapes immediately in the form of hydrogen chloride.

Protocatechuic aldehyde carbonate (m. p.  $124^{\circ}$ ) forms rhombic crystals, and distils at  $162^{\circ}$  (13 mm. pressure), or at  $289^{\circ}$  at atmospheric pressure. Boiling with water leads in a few minutes to quantitative loss of carbonic acid; if 4 parts solution of common salt are used, the protocatechuic aldehyde produced separates out completely on standing in the form of brilliant white crystals.

Citral. C. Harries and A. Himmelmann<sup>1)</sup> report on the behaviour of the two isomeric citrals when treated with ozonised oxygen. When working in petroleum ether solution, bright syrups separate out, which in the dry state form viscid, slightly explosive oils. They correspond to the formula  $C_{10}H_{16}O_5$ , but are probably not uniform monozonides of the above formula, but mixtures of normal ozonides  $C_{10}H_{16}O_4$  (principally), with normal diozonides of the formula  $C_{10}H_{16}O_7$ . This is also showed by their behaviour towards sodium bicarbonate, and also towards water. When heated with water they split up into hydrogen peroxide, lævulic aldehyde, and another aldehyde which could not be identified. The occurrence of acetone peroxide was also observed. Bromine in glacial acetic acid was decolorised by the ozonides; they are consequently unsaturated compounds. The authors conclude from these results that chiefly the ozonide of the formula



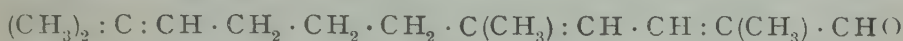
is formed. Diozonides of the two citrals a and b are formed when working in dry carbon tetrachloride. The also form thick syrups, which become solid on standing *in vacuo*, but do not decolorise bromine. When heated with water they split up into acetone peroxide, acetone, lævulic aldehyde, and probably glyoxal, which latter the authors were, however, unable to identify with certainty.



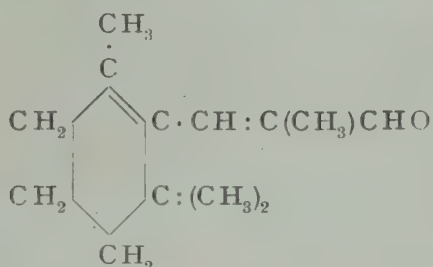
Owing to the great popularity of the natural as well as the synthetic violet preparations in the perfumery trade, further efforts are constantly made to produce synthetically new products which possess the characteristic, delightful violet odour. But up to the present it has not yet been possible to produce a substance which

<sup>1)</sup> Berl. Berichte 40 (1907), 2823.

is superior to ionone, especially as regards its great stability and richness, and also the simplicity of its production. The cyclo-citrylidene propenal recently obtained by Barbier<sup>1)</sup>, which when freshly produced develops a very pleasant flower-like odour strongly reminding of violets, but which has not the cedarwood-like secondary odour peculiar to ionone, also suffers from the fault that it loses already in a short time the freshness and charm of its scent, owing to ready oxidation. By condensing equimolecular quantities of citral and propylic aldehyde in aqueous-alcoholic solution by means of dilute soda liquor, Barbier obtained an unsaturated aldehyde of the formula  $C_{13}H_{20}O$ . The condensation-product appears to consist of two isomeric aldehydes, which boil at 147 to 148° and 158 to 160° (16 mm. pressure) respectively. Its constitutional formula is as follows:—



When treated with 60 per cent. sulphuric acid, at first at a low temperature, subsequently at 50 to 60°, the readily oxidisable aldehyde yields the isomeric cyclic aldehyde of the formula



which like its isomeride ionone, may possibly consist of two isomerides, boiling at 123 to 125° and 132 to 133°. The semicarbazone of the one distillate melts at 174 to 175°; that of the other has hitherto only been obtained in an oily form.

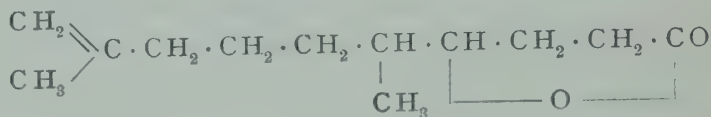
**Citronellal.** In continuation of the work done by Rupe and Lotz<sup>2)</sup>, H. Rupe, S. Pfeiffer, and J. Splittgerber<sup>3)</sup> communicate the results of their studies of condensations with citronellal. According to this, the citronellidene acetic acid of the b. p. 175,5 to 177,5° (14 mm. pressure) first described by the first-named authors, whose melting point was found by Knoevenagel and Grünhagen at 51 to 52°, consists of a mixture of two isomerides. Further experiments namely, have shown that when the assumedly uniform acid of the above-named boiling point is treated with sulphuric acid, a lactone is formed. But from this it is clear that on condensing citronellal with malonic acid,

<sup>1)</sup> Compt. rend. **144** (1907), 1442.

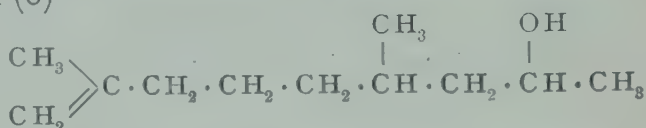
<sup>2)</sup> Berl. Berichte **36** (1903), 2796; Report April 1904, 111.

<sup>3)</sup> Ibidem **40** (1907), 1813.

with application of pyridine, at the temperature of the water-bath, the last-named substance had effected a partial displacement of the double-linking from the  $\alpha$ ,  $\beta$ -position to the  $\beta$ ,  $\gamma$ -position in the molecule of the citronellidene acetic acid. For this reason the authors advise caution in the determination of the constitution of unsaturated acids, which have been obtained by condensation of aldehydes with acids by means of pyridine. The lactone



boils at 161 to 163° (13 mm. pressure) and has a peculiar disagreeable odour. — The authors further produced, by the action of methylmagnesium iodide on citronellal, a secondary alcohol, 2, 6-dimethylnonene-(1)-ol-(8)



The liquid, with a pleasant odour like roses, boiled at 104 to 105° (10 mm. pressure).

With regard to menthocytronellal from menthone by the chemical action of light, see under Physical Notes, p. 123.

## Ketones.

Wallach<sup>1)</sup> and his collaborators have made systematic experiments with reference to the condensation-capability of several terpene ketones with aromatic aldehydes, particulars of which are given in the following notes. Examined were of ketones: cyclopentanone, 1, 2- and 1, 3-methyl cyclopentanone (active), cycloheptanone (suberone), cyclohexanone, 1, 2- and 1, 4- and active and also inactive 1, 3-methyl cyclohexanone; of aldehydes: benzaldehyde, o-, m-, p-nitrobenzaldehyde, o- and p-chlorobenzaldehyde, anisic aldehyde, cuminic aldehyde, piperonal, cinnamic aldehyde, p-dimethylamido benzaldehyde. The conditions of the reaction were as much as possible the same, viz., to an alcoholic solution of the ketone-aldehyde mixture, were added 3 to 5 drops of 8 to 10 per cent. caustic soda liquor. If after 12 to 24 hours no condensation had yet taken place, a few more drops were added. In ketones methylated in ortho-position to the CO-group, 1 molecule aldehyde was employed for every molecule ketone; in all other cases,

<sup>1)</sup> Nachr. K. Ges. Wiss. Göttingen 1907, Meeting of 20. July.

2 mol. aldehyde to 1 mol. ketone. Of the results, the following call for attention: —

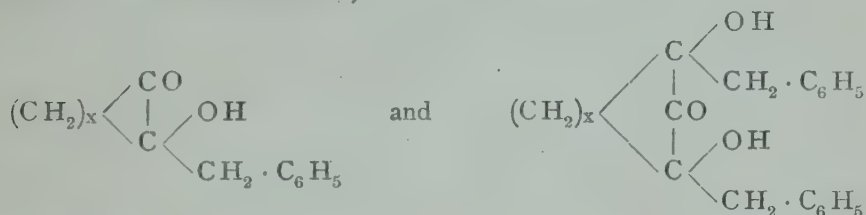
1. In ketones substituted in ortho-position, no condensation occurred with the aldehydes mentioned.

2. Active 1,3-methyl hexanone did not condense with the chlorinated benzaldehydes, whilst the inactive ketone readily yielded a condensation-product under the same conditions. The condensation-products of 1,3-methyl hexanone with *m*- and *p*-nitrobenzaldehyde showed in their active and inactive forms a difference of  $30^{\circ}$  in the melting points, whereas the melting points of the active and inactive condensation-products with the remaining aldehydes lay close together.

3. *O*-, *m*- and *p*-nitrobenzaldehyde showed a large difference in the condensation-capability. The *m*-compound condensed readily, the *p*-compound much more difficultly, and the *o*-compound not at all. On the other hand, *o*-chlorobenzaldehyde readily yielded condensation-products.

4. Under the same conditions the condensation-capability with benzaldehyde decreases from cyclopentanone towards cycloheptanone.

5. When employing benzaldehyde in very dilute aqueous solution and an excess of ketone, it is possible to isolate the intermediate products of the condensation, the aldols: —



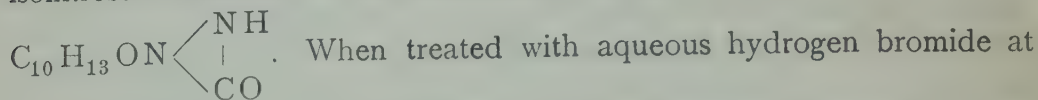
Of these white, readily decomposable compounds, there have been obtained up to the present: from benzaldehyde and cyclohexanone the monoaldol (m. p.  $101$  to  $102^{\circ}$ ) and the dialdol (m. p.  $161$  to  $162^{\circ}$ ); from benzaldehyde and inactive 1,3-methyl hexanone, the monoaldol (m. p.  $106$  to  $107^{\circ}$ ); and from benzaldehyde and 1,4-methyl hexanone, the monoaldol (m. p.  $127^{\circ}$ ).

6. The condensation can also be performed by means of 10 per cent. solution of potassium cyanide. When boiling the aldehyde-ketone mixture with strong formic acid, the condensation also takes place. In this manner it was found possible to condense also the otherwise not reacting *o*-nitrobenzaldehyde with the cyclic ketones.

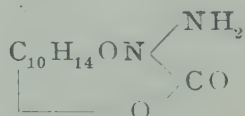
7. The cyclic ketones condensed with two aldehyde radicals, give with concentrated sulphuric acid colour-reactions; the condensation-products of the cyclic ketones with benzaldehyde and the nitrobenzaldehydes dissolve in it with yellow, anisic aldehyde with red, piperonal with carmine red, cinnamic aldehyde with violet coloration.

A table gives a comparative review of the melting points of all the condensation-products formed.

Carvone. In continuation of earlier work<sup>1)</sup> on cyanodihydrocarvone, A. Lapworth studied jointly with E. Wechsler<sup>2)</sup> the behaviour of this compound towards amyl nitrite and sodium ethylate. The product of this reaction, a body melting at 138 to 139°, is not, however, the isonitroso derivative to be expected, but a lactame of the formula



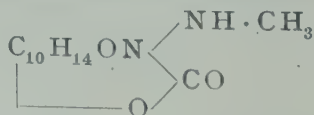
low temperature, it is converted into an isomeric lactame of the m. p. 180°. The first-named body is split up by 10 per cent. caustic soda liquor into an amido acid of the m. p. 155°, which, however, forms back the lactame on heating *in vacuo*, or on boiling with glacial acetic acid or acetic acid anhydride. The methyl ester of the acid is solid, and melts at 99 to 100°. If the lactame of the m. p. 139° remains for several days in contact with concentrated hydrochloric acid, there is formed a lactone base



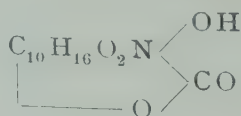
of the m. p. 122 to 123°. The lactame of the m. p. 180°, when treated in the same manner, also yields a lactone base of the m. p. 157 to 158°, isomeric with the former. A methylated lactame is obtained when methyl iodide and sodium methylate are allowed to act on the lactame of the m. p. 139° at the temperature of the water-bath. From this there results, on saponifying with 10 per cent. caustic lye, the methyl-



hydrochloric acid converts the latter in the cold into the methyl lactone base



of the m. p. 129 to 130°. Dilute sulphuric acid converts the last-named base on application of heat, with loss of methylamine, into a lactone acid



of the m. p. 66 to 67°. This acid is identical with the one of the m. p. 70 to 72° formed on hydrolysis of the lactone base by means

<sup>1)</sup> Journ. chem. Soc. 89 (1906), 955, 1819, 1869; Report October 1906, 132; April 1907, 152.

<sup>2)</sup> Ibidem 91 (1907), 977.

of hot dilute sulphuric acid. It also occurs in the reaction of hot dilute sulphuric acid on the above-mentioned lactame, or on the amido acid of the m. p.  $155^{\circ}$ . On continued heating with an excess of concentrated hydrochloric acid, the lactame is converted, with loss of carbonic acid and separation of ammonium chloride, into a dimorphous acid  $C_{10}H_{12}O_2$  of the m. p.  $84^{\circ}$  and  $105$  to  $106^{\circ}$ , which in the authors' opinion probably represents the hitherto unknown 2, 3, 6-trimethyl benzoic acid. Its calcium salt, heated with soda-lime *in vacuo* yields a hydrocarbon boiling at  $166$  to  $168^{\circ}$ , a trimethyl benzene, which Lapworth and Wechsler were able to identify as pseudocumene (2, 3, 6-trimethyl benzene), on the one hand by the tribromide melting at  $224$  to  $226^{\circ}$ , on the other by a mononitro derivative of the m. p.  $70$  to  $71^{\circ}$ , and a trinitro product of the m. p.  $183$  to  $184^{\circ}$ .

**Fenchone.** The fenchone semicarbazone, the production of which had up to the present not yet been accomplished, was obtained by Wallach<sup>1)</sup> in the following manner: 10 g. semicarbazide hydrochloride and 10 g. sodium acetate were dissolved in 20 cc. water, mixed with a solution of 10 g. pure fenchone in 50 cc. alcohol, and left standing for at least a fortnight at the temperature of the room. The alcohol and unconverted fenchone were then driven off with steam, when the semicarbazone remained behind. It crystallised from dilute alcohol in large rhombic prisms of the m. p.  $182$  to  $183^{\circ}$ . d- and l-fenchone showed the same behaviour with regard to the formation of the semicarbazones; a racemic mixture of the two semicarbazones melted at  $172$  to  $173^{\circ}$  and crystallised not so well. The optical rotatory power was as follows: d-fenchone semicarbazone  $[\alpha]_D + 47,04^{\circ}$ , in methyl alcoholic solution; l-fenchone semicarbazone  $[\alpha]_D - 46,88^{\circ}$  in methyl alcoholic solution.

The production of the semicarbazones in the pure state is rendered much more difficult if crude fenchone is used as raw material, as the latter contains impurities which are difficult to remove. For example, a l-fenchone from thuja oil which was considered pure, yielded a semicarbazone with a higher melting point which by recrystallisation from much methyl alcohol could be split up in two fractions, of which one melted at  $238^{\circ}$ , and the other at  $182$  to  $183^{\circ}$ . The ketone regenerated from the higher-melting fraction was found to be l-camphor ( $[\alpha]_D - 39,9^{\circ}$  in ethereal solution). A separation of the camphor from the fenchone is very difficult, and is only rendered possible by the fact that the former reacts much more rapidly with semicarbazide than fenchone.

A more detailed examination by Wallach proved that the camphor is not present as such in thuja oil, but is only formed during the

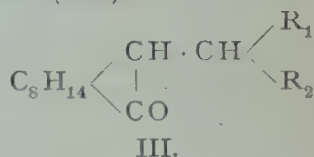
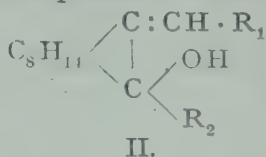
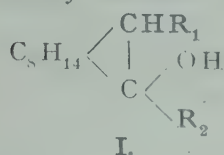
<sup>1)</sup> Liebig's Annalen 353 (1907), 209.

purification of the crude fenchone with nitric acid, owing to oxidation of the l-borneol or its esters present in the oil.

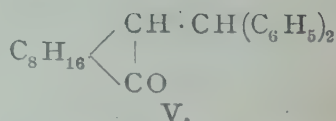
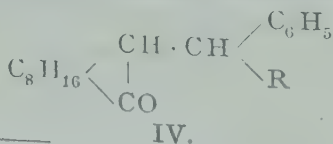
In the d-fenchone of fennel oil, Wallach was also able to state the presence of d-camphor. Whether the latter is contained in the oil as such, or is only formed by oxidation of the borneol or camphene detected in the fennel oil, is a question which cannot be settled without further experiments.

In order to determine the molecular weight of some anorganic compounds, E. Rimini and F. Olivari<sup>1)</sup> have employed fenchone, which readily dissolves various elements and salts, and is suitable for exact measurements, as an ebullioscopic solvent. In an ordinary Beckmann's apparatus with a china-ware jacket the authors have determined for pure fenchone (b. p. 192,5°) the constant  $k$  on the average at 59,4, a value which stands very close to that of menthone ( $k=62,5$ ) and of camphor ( $k=58,5$ ).

Menthone. Haller and Bauer<sup>2)</sup> had vainly endeavoured to arrive by the action of Grignard's salts on ethyl camphor, at bodies of the formula (I.), and attributed the absence of the reaction to a steric impediment. On applying this synthesis to alkylidene compounds of camphor, the authors obtained, instead of the expected tertiary alcohols (II.), compounds of the formula (III.): —



Hydrogen and the alkyl radical of the magnesium organic compound had therefore become attached to the double linking. In connection with this experiment, Boedtker<sup>3)</sup> undertook the examination of the behaviour of ethyl and of benzal menthone. He established that neither ethyl menthone reacts with alkylmagnesium bromides; benzal menthone also behaved like benzal camphor, inasmuch as substitution products of the formula (IV.) were easily formed. In the pure state, namely in the form of two crystallised isomerides, Boedtker only obtained ethyl benzyl menthone, m. p. 102,5 to 103,5°, and 89 to 91°, and the phenyl benzyl derivative (V.) (menthodiphenyl methane): —



<sup>1)</sup> Atti R. Accad. dei Lincei Roma [5] 16, I. 665. Accord. to Chem. Zentralbl. 1907, II. 241.

<sup>2)</sup> Compt. rend. 142 (1906), 677, 971.

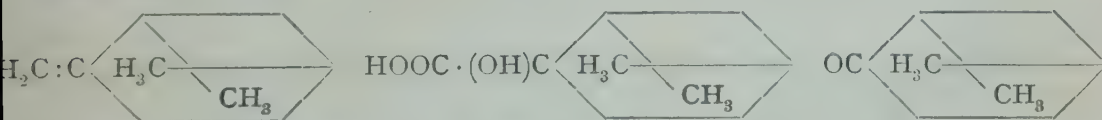
<sup>3)</sup> Ibidem 145 (1907), 329.

occurring in the isomerides, m. p. 139 to 140°, feeble dextrorotation; m. p. 160,5 to 161,5°,  $[\alpha]_D$  in benzene solution  $+158^{\circ}30'$ ; m. p. 136 to 137°, inactive. The analogous methyl, n-propyl, isobutyl, and isoamyl benzylmenthones were syrupy, and, according to the analyses, not yet pure.

Sulphureted reaction-products of menthone with phosphorus trisulphide have been obtained by N. Speranski<sup>1)</sup>. When 1 mol. phosphorus trisulphide is heated with 3 mol. menthone to 140°, there is formed, besides menthene of the b.p. 168 to 170°, thiomenthone  $C_{10}H_{18}S$ , a reddish liquid of peculiar odour, and readily soluble in the usual solvents; b.p. 217 to 220°;  $d_{15^{\circ}} 0,9398$ . This body is decomposed by prolonged standing, with separation of hydrogen sulphide. With alcoholic solution of mercuric chloride, thiomenthone gives a crystalline precipitate. In addition to thiomenthone, there is formed in the above reaction menthene sulphide  $C_{20}H_{34}S$  of the m.p. 50,5° and the b.p. 213° (28 mm. pressure). The compound absorbs 4 atoms bromine. It has not yet been possible to determine the constitution of menthene sulphide. Compounds such as methylhexanone, camphor, etc., also react, according to Speransky, with phosphorus trisulphide.

With regard to the splitting up of menthone by the chemical action of light, see under Physical Notes, p. 124.

Nopinone. A considerable time ago v. Baeyer and Villiger discovered among the oxidation-products of turpentine oil, nopinic acid  $C_{10}H_{16}O_3$ , which on further oxidation yielded the ketone nopinone  $C_9H_{14}O$ . These two bodies, which are derived from the hydrocarbon nopinene ( $\beta$ -pinene) contained in turpentine oil in the following manner: —



have been examined more in detail by Wallach<sup>2)</sup>.

The acid was produced by the following method: 300 g. freshly distilled pinene are shaken with a solution of 700 g. potassium permanganate in 9 litres water, to which 150 g. caustic soda are added. When the oxidation is completed, the unchanged hydrocarbon is distilled off with steam, then the manganese dioxide filtered off, and the filtrate evaporated to 3 litres. On cooling, sodium nopinate crystallises out. The yield is at most 2,5 to 5% of the pinene. Nopinic acid is lævorot-

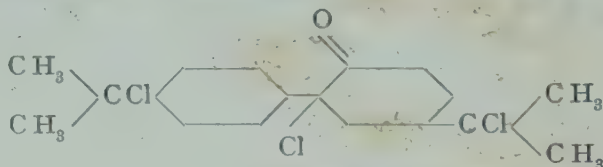
<sup>1)</sup> Journ. Russ. phys.-chem. Soc. **38** (1906), 1346. Accord. to Chem. Zentralbl. **1907**, I. 1746.

<sup>2)</sup> Nachr. K. Ges. Wiss. Göttingen **1907**, Meeting of 8. June.

atory ( $[\alpha]_D - 15,6^\circ$  in ethereal solution), even when it is produced from dextrorotatory turpentine oil. The original hydrocarbon must therefore be the same in dextro- as well as in lævorotatory oils.

In order to obtain nopinone, 10 g. sodium nopinate are dissolved in 100 cc. hot water, and a solution of 3 g. potassium permanganate in 75 g. water added. Next, 2 g. sulphuric acid diluted with 20 cc. water are added, and as soon as the oxidation commences, steam is passed through the liquid, when the nopinone passes over, whose properties are as follows: d. 0,981; b. p.  $209^\circ$ ;  $n_{D20} 1,4787$ ; mol. refr. found 39,87, calculated for  $C_9H_{14}O$  39,51;  $[\alpha]_D + 18,48^\circ$  undiluted,  $+ 37,3^\circ$  in 12 per cent. alcoholic solution,  $+ 11,02^\circ$  in 7,15 per cent. ethereal solution,  $+ 10,79^\circ$  in 7,27 per cent. benzene solution. It solidifies readily in a freezing mixture, and then melts again a little above  $0^\circ$ .

Nopinone condenses readily with benzaldehyde, forming a benzylidene compound melting at  $106$  to  $107^\circ$ , and with itself when hydrochloric acid gas is introduced into its alcoholic solution. The body  $C_{18}H_{29}OCl_3$  formed in the last-named manner has the following constitution: —



Hydrogen chloride has attached itself not only at the double linking formed by the condensation, but also at the bridge bonds of the two tetracyclic rings. The trichloride, decomposing at  $148^\circ$ , splits off readily hydrochloric acid, already when boiled with solvents, and is converted into a dichloride  $C_{18}H_{28}OCl_2$  (m. p.  $125$  to  $126^\circ$ ) which dissolves much more easily in alcohol and ether than the trichloride and which can again be converted into the latter by addition of hydrochloric acid. The ready formation and the difficult solubility of the trichloride can be utilised for the detection of nopinone.

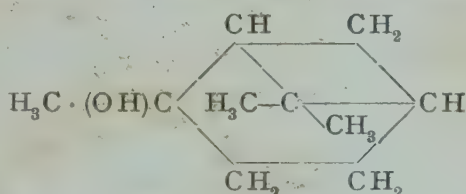
When boiled with dilute sulphuric acid, nopinone is converted into isopropylhexenone (m. p. of the semicarbazone  $183$  to  $184^\circ$ ), which with hydrogen sulphide in alcoholic-ammoniacal solution yields a hydrogen sulphide compound (m. p.  $119^\circ$ ), and is consequently the already known  $\Delta_2$ -isopropylhexenone



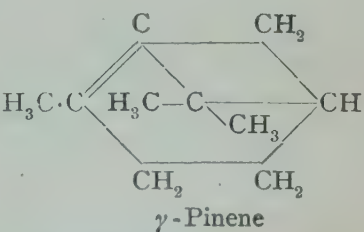
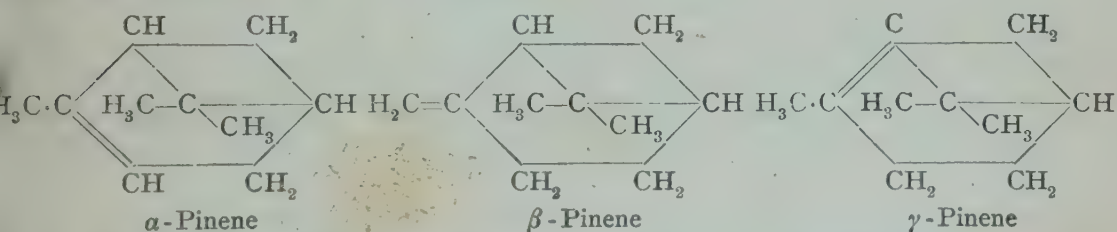
By reduction with sodium in moist ethereal solution, nopinone is converted into the corresponding alcohol nopinol, which exists in two modifications: 1. crystallised  $\alpha$ -nopinol, b. p.  $204$  to  $205^\circ$ ; m. p.  $102^\circ$   $[\alpha]_D - 5,32^\circ$  in 12,53 per cent. ethereal solution; long, readily subliming needles with a camphor-like odour; it remains unaltered on

prolonged contact with dilute sulphuric acid; m.p. of the urethane 131 to 132°. 2. Liquid  $\beta$ -nopinol, a viscid mass from the mother-liquors of the former;  $[\alpha]_D - 15,03^\circ$  in 13,15 per cent. ethereal solution; m.p. of the urethane 95 to 96°. When heated with zinc chloride it gives a bad yield of a hydrocarbon boiling at 157 to 160°, nopinonene, whereas  $\alpha$ -nopinol is much more stable towards zinc chloride. In addition to the two alcohols, there is formed in the reduction of nopinone, the pinacone  $C_{18}H_{30}O_2$  (b. p. 195 to 200° at 11 mm. pressure; m.p. 106 to 107°).

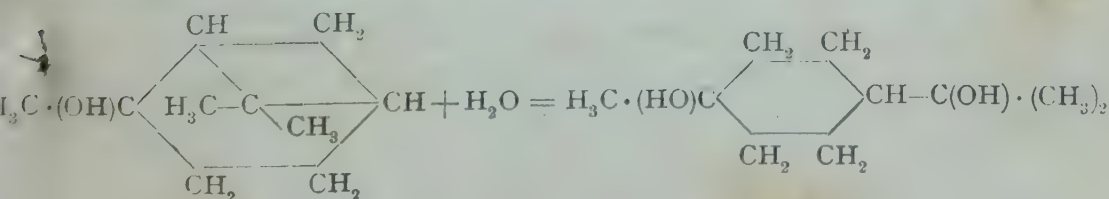
By the action of methyl magnesium iodide on nopinone Wallach obtained homonopinol  $C_{10}H_{17}OH$  (methyl-1-nopinol) of the m.p. 204 to 205°. The pure alcohol forms downy needles melting at 58 to 59° (from dilute methyl alcohol), has the specific rotatory power  $[\alpha]_D - 4,99^\circ$  (in ethereal solution), and possesses according to the manner of its formation, the following constitution: —



It may be looked upon as a hydrate of pinene, and by abstracting water there might be formed from it three hydrocarbons, which Wallach designates as  $\alpha$ -,  $\beta$ - and  $\gamma$ -pinene: —

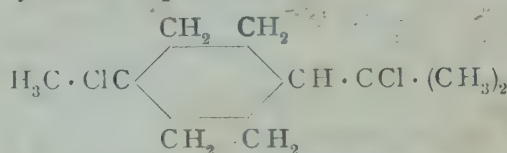


$\alpha$ -Pinene is the ordinary pinene,  $\beta$ -pinene the nopinene hitherto not isolated,  $\gamma$ -pinene can no doubt readily be formed from homonopinol, as a tertiary combined H-atom is present for the abstraction of water. On the other hand, this hydrocarbon will be capable of ready conversion into limonene or terpinolene, with disruption of the tetracyclic ring. The experiment also showed that the tetracyclic ring is split up easily into cis-terpin hydrate, already by shaking homonopinol either with 8 per cent. sulphuric acid, or with cold saturated solution of oxalic acid: —



Attempts to arrive at  $\alpha$ - or  $\beta$ -pinene by the abstraction of water did not lead to the desired result, owing to this behaviour of homonopinol; on the contrary, there were obtained, by means of 85 per cent formic acid, terpenes which gave the terpinene-reaction (nitrite m. p. 153°), the terpinolene-reaction (tetrabromide m. p. 112 to 115°) and the dipentene-reaction (?). From this it may be assumed that during the treatment with formic acid first of all terpin hydrate was formed which then split up into the known decomposition-products dipentene, terpinolene, terpinene, and terpineol. The action of dry agents splitting off water, such as zinc chloride, potassium bisulphate, and soda-lime on homonopinol, led to mixtures of terpene-like hydrocarbons which it has not yet been possible to identify.

The treatment of homonopinol with hydrogen chloride in glacial acetic acid solution yielded dipentene dihydrochloride



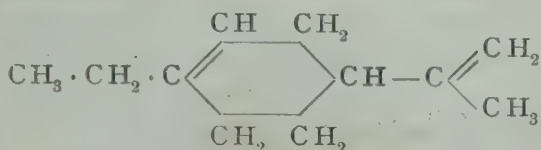
whilst the action of phosphorus pentachloride in ligroin solution in the cold produced the chloride of homonopinol  $\text{C}_{10}\text{H}_{17}\text{Cl}$ . It boiled at 95 to 105° (13 mm. pressure) or 200 to 205° at atmospheric pressure, with loss of hydrochloric acid, and consequently differed completely from pinene hydrochloride. This is a fresh proof that in adding hydrogen chloride to dry pinene, in the first phase not the double bond is dissolved, but the tetracyclic ring is broken up. If the glacial acetic acid solution of the chloride is saturated with hydrochloric acid, dipentene dihydrochloride is also formed. With amylnitrite and nitric acid, homonopinol chloride yields a chlorinated nitrosate.

Analogous to homonopinol, Wallach produced from nopinone and ethyl magnesium iodide ethyl nopinol  $\text{C}_{11}\text{H}_{20}\text{O}$  (m. p. 43 to 45° b. p. 219 to 223°), which on heating with formic acid yielded, with loss of water, homologous terpenes, and on shaking with 5 per cent sulphuric acid was converted into a homologous terpin hydrate  $\text{C}_{11}\text{H}_{22}\text{O}_2 + \text{H}_2\text{O}$  (m. p. 75 to 76°).

By saturating ethyl nopinol<sup>1)</sup> with hydrohalogenides in glacial acetic acid solution, or by treating homo-cisterpin hydrate in glacial acetic acid solution with hydrohalogenides, the corresponding dihalogen derivatives were formed: dihydrochloride of the m. p. 63 to 64°, dihydrobromide of the m. p. 82 to 84°, dihydriodide of the m. p. 63 to 64°. From the dihydrochloride there was obtained by abstraction of hydrochloric acid by means of aniline, the hydrocarbon  $\text{C}_{11}\text{H}_{18}$  (b. p. 201 to 202°; d 0,8545

<sup>1)</sup> Nachr. K. Ges. Wiss. Göttingen 1907, Meeting of 20. July.

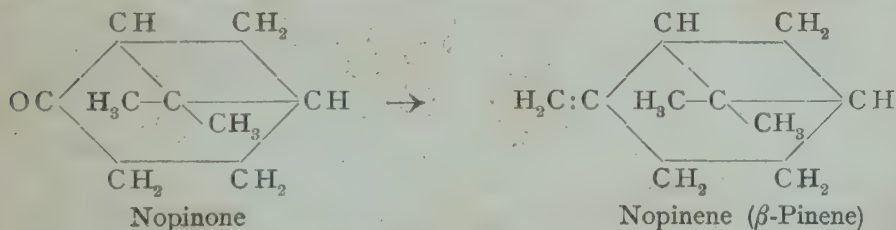
$n_{D18} 1,4802$ ; mol. refr. found 49,89, calculated for  $C_{11}H_{18} / \sqrt{2}$  49,84), which yielded a solid tetrabromide (m. p. 124 to 125<sup>o</sup>) and a readily soluble nitrosochloride which could be converted into an oxime and further into a ketone with a carvone-like odour. But these bodies have not been examined further. From the above-described behaviour it is clear that the hydrocarbon  $C_{11}H_{18}$  consists chiefly of the higher homologue of dipentene: —



The formation of the higher homologues did apparently not proceed as easily as that of methyl and ethyl nopinol. At any rate, the yield of n-propyl nopinol was bad, as owing to secondary reactions much nopinone had been converted into nopinol.

With regard to analogous reactions of sabina ketone, see under Terpinene, p. 142.

In order to obtain a knowledge of the properties of the nopinene ( $\beta$ -pinene) which is present in turpentine oil but has not yet been isolated, Wallach attempted the synthetic production of this body. The crude material used was nopinone, which by the method indicated by Wallach for the formation of methene hydrocarbons (which has already repeatedly been described) should lead to nopinene ( $\beta$ -pinene):



Nopinone was converted with bromoacetic ester and zinc into the corresponding hydroxy ester, and the latter by abstraction of water with potassium bisulphate into the unsaturated ester. The acid (b. p. 190 to 210<sup>o</sup> at 13 mm. pressure) obtained by saponification of the latter, yielded on distillation at ordinary pressure a terpene  $C_{10}H_{16}$ , of which the bulk boiled at 158<sup>o</sup> (d 0,8630;  $[\alpha]_D + 15,93^\circ$ ;  $n_{D20} 1,4699$ ; mol. refr. found 43,96, calculated for  $C_{10}H_{16} / \sqrt{2}$  43,53, for  $C_{10}H_{16} / \sqrt{2}$  45,24). The physical constants show that this is a bicyclic hydrocarbon with one double bond. It possesses a pronounced turpentine odour, and contains a methene-group, as may be assumed from the oxidation-products. The terpene was oxidised under the conditions mentioned for the formation of nopinic acid (see p. 161) when in a good yield a sodium salt was obtained, which resembled the sodium nopinate

from turpentine oil. It has the same composition as the latter, but is somewhat, better soluble and is dextrorotatory, whereas the one from turpentine oil is lævorotatory. The acid liberated from the salt has the m. p. 154 to 155° (from benzene), and is stable towards hot 12 per cent. sulphuric acid, contrary to nopinic acid which yields hydrocuminic acid. It is also a hydroxy acid, as is shown by the oxidation, which was carried out as in the case of nopinic acid. But the ketone  $C_9H_{14}O$  differs from nopinone. It is solid (m. p. about 60°) and possesses an odour reminding of camphenilone and fenchocamphorone. M. p. of the semicarbazone 206 to 207°.

The synthetic terpene could be converted with glacial acetic and sulphuric acids, according to Bertram and Walbaum, into the crystallised alcohol  $C_{10}H_{18}O$  (m. p. 62 to 63°; b. p. 202 to 204°) which has a camphor-like odour, and which on oxidation with chromic acid yielded a ketone  $C_{10}H_{16}O$  solidifying at a very low temperature, whose semicarbazone melts at 220 to 221°. This behaviour reminds strongly of the hydrocarbons obtained by Aschan<sup>1)</sup> from the liquid hydrochlorides from turpentine oil.

From the observations communicated, Wallach draws the conclusion that the synthetic hydrocarbon from nopinone differs physically and probably also chemically from the nopinene ( $\beta$ -pinene) of turpentine oil which supplied the nopinone used for the synthesis. For this reason it is believed that in the formation of the artificial terpene from nopinone, a configuration-displacement occurs.

Methylcyclohexanone. W. Markownikow and W. Smirnow<sup>2)</sup> have worked on some derivatives of  $\beta$ -methylcyclohexanone, with the view of arriving at a suitable crude material for the production of hexahydro-m-toluylic acid. The most suitable for this purpose appeared to be the hydroxy acid corresponding to  $\beta$ -methylcyclohexanone, which could be produced in the most practical manner by the following method. The cyanohydrin of  $\beta$ -methylcyclohexanone (m. p. 63 to 64°) is dissolved with cooling (— 15°) in 3 parts concentrated sulphuric acid; after 24 hours' standing this is diluted with water, and in this manner an amide  $C_8H_{15}O_2N$  (m. p. 120 to 121°) is obtained, from which by heating with dilute sulphuric acid (d 1,32) the corresponding hydroxy acid  $C_8H_{14}O_3$  (b. p. 163 to 166° [12 mm. pressure], 260 to 270° with partial decomposition [733 mm. pressure]), is readily formed. This acid, however, consists apparently of two isomerides, for on heating with aniline (molecular quantities) there are obtained two ævorotatory anilides of the m. p. 90 to 91° and 118,5 to 119,5°.

<sup>1)</sup> Comp. the present Report, p. 136.

<sup>2)</sup> Journ. Russ. phys.-chem. Soc. 39 (1907), 1. Accord. to Chem. Zentralbl. 1907. I. 1407.

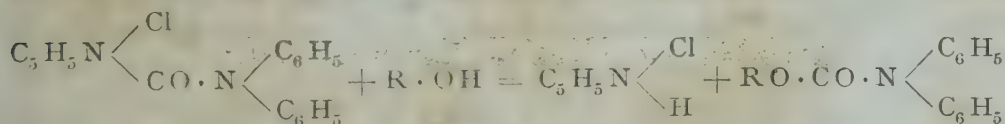
respectively, which can be separated by petroleum ether. Up to the present it has not yet been possible to effect a reduction of the hydroxy acid into hexahydro-m-toluylic acid by heating with red phosphorus and hydriodic acid.

With regard to p-nitrobenzyl mercaptan as a reagent on ketones, see under Aldehydes, p. 151.

### Phenols and Phenol Ethers.

Whilst up to the present diphenyl urea chloride could only be employed in a few cases for the determination of the alcoholic hydroxyl group, J. Herzog<sup>1)</sup> recommends this reagent as specially adapted for detecting phenols, as it readily forms well-crystallising compounds with the latter. Tertiary alcohols do not as a rule react with diphenyl urea chloride, whose behaviour therefore shows a characteristic difference with the hydroxyl groups of the alcohols, and the phenols. Of all the phenols and derivatives of phenols which Herzog employed for the formation of urethanes, only the phenol carboxylic acids do not react easily with diphenyl urea chloride, as the free carboxyl group impedes the reaction. Salicylic acid, for example, does not yield a urethane, but salol does. For the production of the phenol urethanes Herzog gives the following directions: The phenol, with four times the quantity pyridine and the molecular weight of diphenyl urea chloride, is heated in a flask provided with a reflux tube for an hour in boiling water; the solution is then whilst stirring poured in water, when a reddish, more or less greasy crystalline paste separates off, which is recrystallised from ligroin or alcohol.

The reaction occurs probably in the following manner: the diphenyl urea chloride forms first of all with the pyridine, diphenyl urea pyridine chloride, which is then split up in the presence of phenols into pyridine hydrochloride and phenol urethane.



Herzog gives the following reasons for this supposition: in dissolving diphenyl urea chloride in pyridine, he obtained, with a vivid red coloration, diphenyl urea pyridine chloride, which on recrystallisation from an anhydrous mixture of alcohol and ether can be obtained in colourless needles which soon acquire a red colour when exposed to the light. These needles become soft at 105°, and melt at 110° with evolution of gas. As this product gives with phenols the corre-

<sup>1)</sup> Berl. Berichte 40 (1907), 1831.

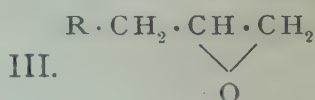
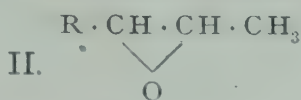
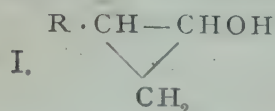
sponding urethanes in a better yield than diphenyl urea chloride itself, it must no doubt be considered as an intermediate product in the above reaction.

The diphenyl urethanes can very readily be saponified. The formation of urethanes is suitable for the purification and identification of phenols; the yield fluctuates between 70 and 90% of the quantity calculated theoretically.

Of the phenol-diphenyl urethanes produced there may be mentioned eugenol diphenyl urethane  $(C_6H_5)_2N \cdot CO \cdot O \cdot C_{10}H_{11}O$ , m. p. 107 to 108°.

With regard to the determination of hydroxyl groups according to Zerewitinoff, see under Analytical Notes, p. 117.

In the numerous treatises by Pond, Hell, and Hoering, which we have discussed from time to time, it has been shown that in the dibromides of the aromatic propenyl ethers, the bromine atom which is situated nearest to the benzene-nucleus is readily exchanged for OH and other radicals. Tiffeneau and Daufresne found<sup>1)</sup> that the dibromides of the isomeric allylphenyl ethers  $R \cdot CH_2 \cdot CHBr \cdot CH_2Br$  behave in an analogous manner; when heated with alcoholic potassium acetate, they exchange the bromine atom next to the benzene nucleus for  $OCOCH_3$ , and yield acetobromohydrins. When these are boiled with alcoholic potash, they split off acetyl and bromine and are converted in substituted cyclopropanols (I), whilst the acetobromohydrins of the isomeric propenyl derivatives in such case of course yield ethylene oxides (II). From these oxides, and the isomeric oxides (III),



the cyclopropanols, like the corresponding acetates, differ by their specific gravity, which is about 0.06 units higher, but chiefly by the fact that they can be converted into substituted hydratropic aldehydes



under the same conditions under which the oxides are converted into arylacetones  $R \cdot CH_2 \cdot CO \cdot CH_3$  and hydrocinnamic aldehydes  $R \cdot CH_2 \cdot CH_2 \cdot CHO$  respectively. From the allyl dibromides directly, the hydratropic aldehydes (and also cyclopropanols) are formed by boiling with aqueous potash solution. The following derivatives of estragol and safrol were produced:

1. Estragol. Dibromide (by brominating in a cold solution of carbon disulphide):  $d_{17} 1.639$ , b. p. 188 to 192° (18 mm. pressure);

<sup>1)</sup> Compt. rend. 144 (1907), 924.

acetobromohydrin:  $d_{00} 1,249$ , b. p.  $160^{\circ}$  with decomposition (13 mm. pressure); cyclopropanol: b. p. of the crude fraction 145 to  $160^{\circ}$  (15 mm. pressure), m. p.  $79^{\circ}$ ; acetate of the cyclopropanol:  $d_{00} 1,123$ , b. p. 164 to  $165^{\circ}$  (13 mm. pressure); hydratropic aldehyde:  $d_{00} 1,089$ , b. p. 253 to  $255^{\circ}$ ; oxime: m. p.  $98^{\circ}$ ; semicarbazone: m. p.  $136^{\circ}$ ; hydratropic acid: m. p.  $58^{\circ}$ .

2. Safrol. Cyclopropanol:  $d_{00} 1,286$ , b. p. 170 to  $178^{\circ}$  (15 mm. pressure); acetate,  $d_{00} 1,255$ ; oxime of the hydratropic aldehyde: m. p.  $71^{\circ}$ ; semicarbazone: m. p.  $158^{\circ}$ .

The formation of aldehydes and ketones from  $\alpha$ -glycols is accomplished (as Tiffeneau has demonstrated in various earlier works), in the first case without displacement of linkings, in the second with such, according to the following formulæ: —

1. Re-arrangement without linking-displacement:



2. Re-arrangement with linking-displacement:



A migration of carbon atoms consequently occurs only if the more stable of the two hydroxyl radicals is situated in proximity to the aryl rest. A typical example of such a re-arrangement is the formation of diphenylacetic aldehyde from hydrobenzoin.

In view of the conversion (observed by Balbiano and Paolini)<sup>1)</sup> of  $\alpha$ -glycols into hydrocinnamic aldehydes (by means of  $\text{ZnCl}_2$ ): —



although these were not clearly identified, and whose oximes and semicarbazones showed melting points which agreed rather with those of the arylacetone derivatives (Wallach, Hoering, Béhal and Tiffeneau) than with those of the derivatives of hydrocinnamic aldehyde (Fourneau and Tiffeneau), — Tiffeneau and Daufresne<sup>2)</sup> undertook to test the reaction mentioned above under No. 1, for its general applicability.

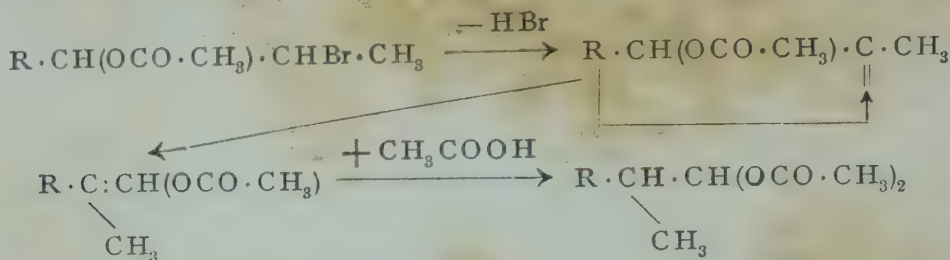
The glycols were obtained from the dibromides of the propenyl ethers through the acetobromohydrins, which on treatment with acetates of heavy metals (Ag, Pb) yielded partly bromophenyl ethers, and partly glycol diacetates. The derivatives hitherto produced from anethol had the following constants: acetobromohydrin:  $d_{00} 1,460$ , b. p. 180 to  $185^{\circ}$  (14 mm. pressure); bromopropenyl ether:  $d_{00} 1,325$ ,

<sup>1)</sup> Comp. Report April 1906, 100.

<sup>2)</sup> Compt. rend. 144 (1907), 1354.

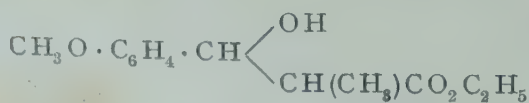
b. p. 153 to 154° (15 mm. pressure); diacetate of the glycol:  $d_{20} 1,127$ , b. p. 187 to 189° (12 mm. pressure).

When the acetic acid solution of anethol dibromide was boiled with zinc acetate, there was unexpectedly formed, by means of re-arrangement, p-methoxyhydratropic aldehyde, whose occurrence is provisionally explained by the authors by the following formulæ: — ( $R = CH_3 \cdot O_6 H_4$ ).



The anethoglycol of the m. p. 116° obtained from the glycol diacetate, proved to be identical with the  $\alpha$ -glycol of the m. p. 114 to 115°, produced from anethol directly (by oxidation with mercuric acetate) in addition to a  $\beta$ -isomeride of the m. p. 62 to 63°. On distillation *in vacuo* the glycol split off water, and was converted into a body melting at 98°, and boiling between 240 and 250° (14 mm. pressure), to all appearances a derivative of diethylene oxide. When treated with 20 per cent. sulphuric acid, the glycol yielded anise ketone  $CH_3 O \cdot C_6 H_4 \cdot CH_2 \cdot CO \cdot CH_3$  (m. p. of the oxime 74°, of the semicarbazone 175°). It is a very remarkable fact that Varenne and Godefroy<sup>1)</sup> obtained an anethoglycol from anethol dibromide by treatment with alcoholic potash, that is to say, under conditions, under which, according to Wallach and Pond, the ketone  $CH_3 O \cdot C_6 H_4 \cdot CO \cdot CH_2 \cdot CH_3$  should have been formed.

New syntheses of anethol and isosafrol have been carried out by Wallach and Evans<sup>2)</sup>. As crude material they employed anisic aldehyde and piperonal respectively. Anisic aldehyde was condensed in benzene solution with bromopropionic acid ester; from the hydroxy ester formed



(b. p. 235 to 245° at 35 mm. pressure) water was abstracted by means of potassium bisulphate at 150°, and the unsaturated ester obtained (b. p. 170 to 180° at 25 mm. pressure) was saponified. The acid

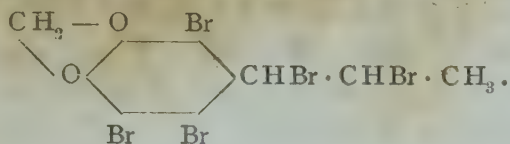
<sup>1)</sup> Compt. rend. **140** (1905), 591; Report October **1905**, 119.

<sup>2)</sup> Nachr. K. Ges. Wiss. Göttingen **1907**, Meeting of 20. July.

formed (m.p.  $157^{\circ}$ ) split up on slow distillation into carbonic acid and anethol.

Piperonal, when treated in exactly the same manner, yielded, though not quite readily, isosafrol.

Isosafrol. In continuation of his work on the dibromides of aromatic propenyl compounds<sup>1)</sup>, Hoering<sup>2)</sup> examined the behaviour of the hitherto not produced tribromo isosafrol dibromide



Whereas in the case of anethol it had not been possible, even by energetic bromination, to introduce more than two bromine atoms into the nucleus, it was found that under certain conditions in isosafrol all three hydrogen atoms in the nucleus could be replaced by bromine, if isosafrol was allowed to drop into a large excess of bromine, and the reaction-temperature was maintained at about  $30$  to  $35^{\circ}$ . Under such conditions only the tribrominated dibromide, briefly called "isosafrol pentabromide", of the m. p.  $196,5$  to  $197^{\circ}$ , was formed; but if the brominating took place at  $60$  to  $63^{\circ}$ , so that vapours of bromine and hydrogen bromide escaped, there was almost exclusively formed the well-known dibrominated isosafrol dibromide of the m. p.  $129$  to  $130^{\circ}$ . The reaction-capacity of the pentabromide, which finds expression particularly in the readiness with which the dibrominated side-chain is attacked, has become much reduced in comparison with that of the lower-brominated derivatives; thus, the body no longer reacted with aqueous acetone, with alcohol, concentrated hydrobromic acid, and alcoholic potash; also when treated with fusing potash or with chromic acid and glacial acetic acid, the bulk of the pentabromide remains unchanged. On oxidation with permanganate, there was formed, by secondary alkali action, a small quantity of tribrominated isosafrol oxide. On the other hand, the two bromine atoms in the side-position could be removed by reduction by means of zinc dust in benzene-alcoholic solution, with formation of the tribromo isosafrol  $\text{C}_6\text{Br}_3(\text{O}_2\text{CH}_2)\text{CH}:\text{CH}\cdot\text{CH}_3$  of the m. p.  $110$  to  $111^{\circ}$ , which is very stable towards permanganate. The same reaction could also be carried out with di- and monobromo isosafrol dibromide. When treated with bromine, tribromo isosafrol yielded back pentabromide; in sunlight, the original pentabromide was formed; but a new not yet further

<sup>1)</sup> Berl. Berichte **37** (1904), 1542; **38** (1905), 2296, 3458, 3464, 3477. Report October 1904, 11; October 1905, 117; April 1906, 132.

<sup>2)</sup> Ibidem **40** (1907), 1096.

examined stereo-isomeride resulted if the work was carried on in diffused daylight, or in the dark. With hydrogen iodide and phosphorus, the pentabromide is reduced into tribromo dihydrosafrol of the m. p. 73 to 74°. Contrary to isosafrol pentabromide, tribromo isosafrol could be split up, by means of alcoholic potash under pressure, into tribromo ethoxy-isoeugenol:  $C_6Br_3(CH:CH \cdot CH_3)^1(OCH_2 \cdot OC_2H_5)^3(OH)^4$  of the m. p. 96 to 99°, which, when heated with very dilute acids, yielded tribromo propenylpyrocatechol in of the m. p. 111 to 113°. Of both bodies the corresponding methyl and acetyl derivatives were produced.

The conversions of the bromine atoms in the side-position of the pentabromide were accomplished in the same manner as in the case of the lower-brominated compounds.

E. Rimini and F. Olivari<sup>1)</sup> have submitted myristicin and isomyristicin to the action of Bougault's reagent. When employing an alcoholic solution of 12 g. myristicin, on which they allowed to act 7 to 8 g. yellow mercuric oxide and 17 g. iodine, they obtained, after filtering and adding potassium iodide and sodium bisulphite, a colourless oil of the composition  $C_{11}H_{13}IO_4$ . Two mol. isomyristicin, when treated in an analogous manner with 1 mol. mercuric oxide and 4 mol. iodine, also yielded an oily isomeric iodine compound.

When double the quantity mercuric oxide is employed, isomyristicin yields an oily product, which combines with bisulphite, and yields the semicarbazone of methoxy methylenedioxy hydratropic aldehyde of the m. p. 140°. The aldehyde liberated from this boiled without decomposition at 288 to 290° (ordinary pressure). As on oxidation of isomyristicin in alcoholic solution, large quantities acetal are formed, it is advisable to use ether saturated with water, in place of alcohol. The examinations confirm the view that myristicin and isomyristicin contain an allyl and propenyl chain respectively.

In connection with earlier work done by Thoms<sup>2)</sup>, O. Richter<sup>3)</sup> gives some brief information on his researches with the object of elucidating the constitution of myristicin and its derivatives. On reducing myristicin with sodium and alcohol, Thoms had obtained two new compounds, viz., dihydromyristicin and a phenol which he converted by methylating into its methyl ether. He assumed that in splitting up isomyristicin, the oxygen atom situated in para-position towards the propenyl-group, is displaced, but he was unable to supply a direct proof in support of this. Richter now attacked this problem, by oxidising the unsaturated side-chain of the phenol ether with potassium

<sup>1)</sup> Atti R. Accad. dei Lincei, Rome [5] 16, I. 663. Accord. to Chem. Zentralbl. 1907, II. 234.

<sup>2)</sup> Berl. Berichte 36 (1903), 3446; Report April 1904, 67.

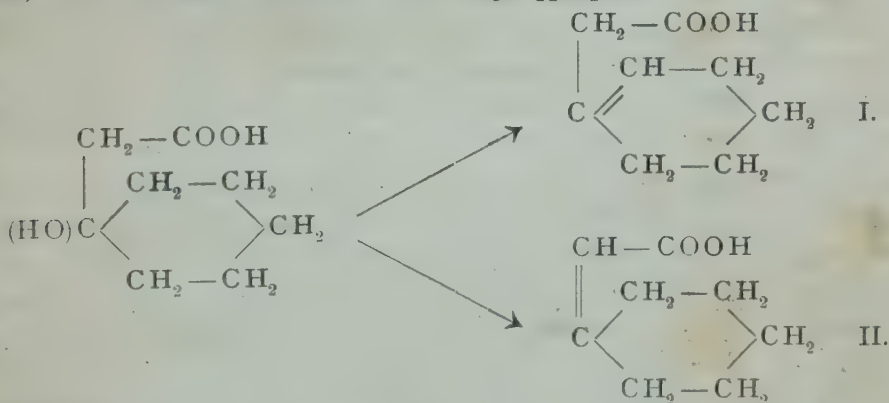
<sup>3)</sup> Bericht d. deutsch. pharm. Ges. 17 (1907), 152.

permanganate (calculated for 1 mol. phenol ether 5 atoms oxygen) into the carboxyl group, when he obtained white needles of the composition  $C_9H_{10}O_4$ , whose melting point lay at  $182^\circ$ , that is to say about the melting point of veratric acid. If Thoms' view were correct, dimethyl- $\alpha$ -resorcylic acid should have been formed, or otherwise, if the methylenedioxy group had been split up in the reverse direction, veratric acid ought to have been formed. Richter now succeeded in establishing the identity of the above acid with dimethyl- $\alpha$ -resorcylic acid, and to correct the statements found in the literature. The dimethyl- $\alpha$ -resorcylic acid obtained by Richter from methylated orcin by oxidation, also melted at  $182^\circ$ , and not, as stated in the literature, at  $175$  to  $176^\circ$ . On mixing the two acids the melting point was not depressed, so that the acid obtained from the methylated phenol ether is identical with dimethyl- $\alpha$ -resorcylic acid. This also proves that on splitting up isomyristicin, the oxygen atom situated in para-position towards the propenyl-group is removed, and that the methoxyl-group originally existing in myristicin stands in meta-position towards the allyl-group, which proves the possibility of converting myristicin acid into gallic acid. The constitution which Thoms accepted for myristicin, is therefore correct.

### Acids.

Wallach<sup>1)</sup> has produced a series of acids which can be derived from simple cyclic hydrocarbons, and has described them and a large number of their derivatives. They contain the radicals cyclopentyl-,  $C_5H_9$ -, cyclohexyl-,  $C_6H_{11}$ -, methylcyclohexyl-,  $C_7H_{13}$ -, cycloheptyl-,  $C_7H_{13}$ -, and menthyl-,  $C_{10}H_{19}$ -, and are designated by Wallach as "cycloalkyl", or briefly as "cyclyl"-acetic acids.

1. Compounds from cyclohexanone. Cyclohexanol acetic ester  $C_{10}H_{18}O_3$ <sup>2)</sup> yields, after abstraction of water and subsequent saponification, two isomeric hexenic acids  $C_8H_{12}O_2$ : —



<sup>1)</sup> Liebig's Annalen **353** (1907), 284.

<sup>2)</sup> Ibidem **347** (1906), 329; Report April 1906, 129; October 1906, 115.

A small quantity is formed of an acid, volatile with steam, of the m. p. 91 to 92°. On oxidation it yields cyclohexanone and it has therefore the formula II ( $\Delta_{1,7}$ -cyclohexene acetic acid). With glacial acetic and hydrobromic acids it yields the same addition-product (m. p. 89 to 90°) as the non-volatile acid (m. p. 38°), which is formed in the larger proportion, and to which Wallach provisionally allots the formula I ( $\Delta_{1,2}$ -cyclohexene acetic acid). In like manner, hexanol acetic acid yields the same compound if treated with glacial acetic acid and hydrobromic acid. In both isomeric acids the double linking is consequently attached to the same carbon atom. Oxidation of the hexenic acid (m. p. 38°) with potassium permanganate led to an aldehyde (or ketone) of the formula  $C_7H_{10}O$ , which could be further oxidised with silver oxide into glutaric acid. The peculiar progress of this oxidation, which it is intended to study still further, induced the author to refrain for the present from an interpretation. Cyclohexyl acetic acid, corresponding to the unsaturated acids, was produced in this manner, that cyclohexanol acetic ester was dissolved in glacial acetic and hydrobromic acids, the bromide formed after 48 hours reduced directly with zinc dust, and the resulting ester saponified. The crude acid obtained contained unsaturated hexenic acids, which were removed by oxidation with potassium permanganate. Cyclohexyl acetic acid  $C_8H_{14}O_2$  is stable towards permanganate, melts at 30 to 31°, and boils at 245 to 247° without decomposition. Besides various derivatives of the acid, there were produced by distillation of calcium cyclohexylacetate *in vacuo*, completely hydrated dibenzyl ketone



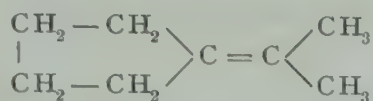
and in the same manner, from calcium acetate and calcium cyclohexyl acetate, cyclohexyl acetone (b. p. 198 to 200°).

2. Compounds from suberone. Suberyl acetic acid (cycloheptyl acetic acid) was obtained from suberol acetic ester<sup>1)</sup> in an analogous manner to cyclohexyl acetic acid. It boils at 165° (19 mm pressure) and has an unpleasant odour like fatty acids.

3. Compounds from cyclopentane. Cyclopentyl acetic acid, also produced in the same manner, boils at 226 to 230°, and has an odour like fatty acids. Cyclopentene isobutyric acid was produced from pentanol isobutyric acid ester (from pentanone bromoisobutyric acid ester, and zinc) by means of potassium bisulphate (b. p. 148 to 150° at 27 mm. pressure). It is converted by distillation at ordinary pressure, with loss of carbonic acid, into

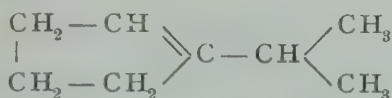
<sup>1)</sup> Liebig's Annalen **345** (1906), 146; Report October 1906, 145.

a hydrocarbon  $C_8H_{14}$  (b. p. 136 to 137°,  $d_{20} 0.817$ ,  $n_D 1.4581$ ), which must consist chiefly of a compound of the formula



as it yields pentanone<sup>1)</sup> on oxidation.

When treated with alcoholic sulphuric acid, it is converted into the isomeric hydrocarbon



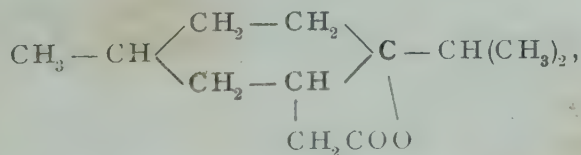
from which a solid nitrosochloride was obtained, whereas the former only yielded an oily product.

4. The constitution of 1,4-methyl cyclohexene acetic acid of the m. p. 42 to 43°<sup>2)</sup> which had already been produced before, could be ascertained by oxidation into methylcyclohexanone as



The saturated 1,4-methyl cyclohexyl acetic acid (m. p. 63 to 65°) was obtained like the above-mentioned cyclohexyl acetic acid.

5. Compounds of menthone. Methyl ester of menthol acetic acid was obtained from menthone, bromoacetic ester, and zinc; m. p. 32 to 33°; b. p. 136 to 137° (10 mm. pressure). Menthol acetic acid (m. p. 82 to 83°, b. p. 193 to 197° (11 mm. pressure). On producing from this acid menthene acetic acid, by abstracting water by means of potassium bisulphate, there is formed as a by-product the  $\gamma$ -lactone  $C_{12}H_{20}O_2$  (b. p. 300 to 305°,  $d 1.015$ ,  $n_D^{22} 1.4781$ ; lævorotatory) of the following constitution:—

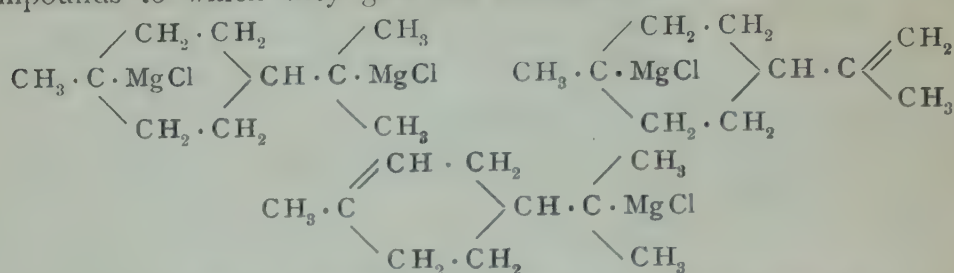


which on treatment with glacial acetic and hydriodic acids is converted into an isomeric dextrorotatory solid lactone of the m. p. 88 to 89°. Menthyl acetic acid was produced from bromomenthyl acetic ester by reduction and subsequent saponification, analogous to cyclohexyl acetic acid (b. p. 166 to 170°, at 11 mm. pressure).

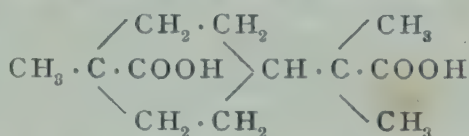
<sup>1)</sup> According to Wallach, the semicarbazone of pentanone melts at 205 to 206° if heated slowly, and at 212 to 213° if heated rapidly.

<sup>2)</sup> Liebig's Annalen **347** (1906), 345; Report October **1906**, 115.

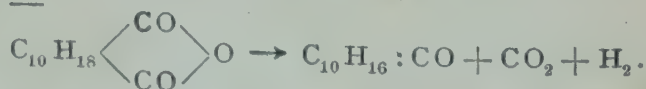
By the action of magnesium on dipentene dihydrochloride dissolved in ether, Barbier and Grignard<sup>1)</sup> obtained three organomagnesium compounds to which they give the formulæ: —



There was further formed by splitting off hydrochloric acid, a fair quantity of a terpene boiling about 171 to 175°, probably dipentene. If the mixture of the magnesium compounds is treated with carbon dioxide, and worked up in the usual manner, there results a mixture of three acids; one dibasic, and two monobasic acids. If the ethereal solution of the acids and the terpene is shaken with sodium bicarbonate solution, the dicarboxylic acid separates off (i. e., passes over into the bicarbonate solution?); the monocarboxylic acids can only be abstracted from the ether by means of dilute soda solution. In this examination the authors only took the dicarboxylic acid into consideration, and they gave to it the formula of a menthane-1,8-dicarboxylic acid: —



This acid exists in two stereoisomeric forms; the cis-modification represents a powder of small crystals of the m. p. 192° (uncorr.), only slightly soluble in cold water; the cis-trans-form, much more readily soluble, but otherwise resembling the cis-form, melts at 174 to 175°. The cis-acid, boiled with acetic anhydride, yields an anhydride soluble in chloroform, which can be precipitated by ligroin; m. p. 145 to 148° (in a sealed tube). If this anhydride is heated in accordance with Blanc's<sup>2)</sup> directions to 250 to 350°, there is formed a viscous oil, from which by rectification *in vacuo* a ketone-like body C<sub>11</sub>H<sub>16</sub>O was isolated: —

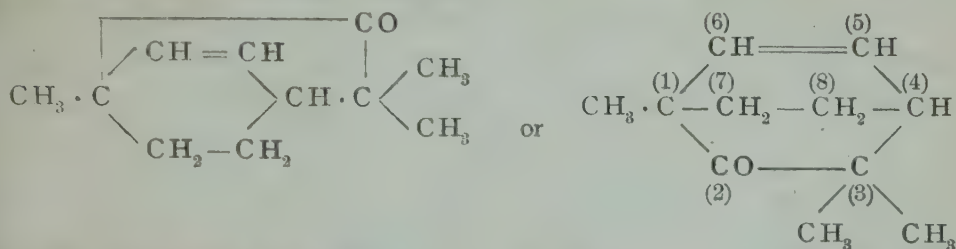


The ketone is a light, green-yellow, oil with a strong camphor odour, which is very mobile even at a low temperature, with the following constants: b. p. 93 to 95° (13 mm. pressure); d<sub>0°</sub> 0,9886; d<sub>12,9°</sub> 0,9783; n<sub>D</sub> 1,49018; mol. refr. found 48,48, calculated 48,32.

<sup>1)</sup> Compt. rend. **145** (1907), 255.

<sup>2)</sup> Ibidem **144** (1907), 143.

The oxime of the ketone boils at 16 mm. pressure about 138 to 140°, and when recrystallised from a mixture of ether and petroleum ether, melts at 150 to 151°. Barbier and Grignard ascribe to this ketone the following formula:



and they designate it as trimethyl-1, 3, 3-bicyclo-1, 7, 8, 4-hexene-5-one-2; they consequently look upon the bridge as a special substituent, the original ring thereby becoming more manifest.

### Nitrogenous Bodies.

The generally accepted view that the nitrites of primary amines of the aliphatic series are unstable compounds which decompose the moment they are formed, is opposed to by Wallach<sup>1)</sup> in his treatise On the behaviour of nitrites of primary bases, and on the ring-enlargement of carbocyclic systems. He proves that these bodies, and particularly those of the primary alicyclic bases, when every trace of free acid is kept away, are partly so stable, that they can be recrystallised from hot water. On the other hand, the smallest quantity of free acid has in a high degree a decomposing action. For example, the very stable recrystallised nitrites of l-menthylamine (decomposing point 139°) and of pinylamine (decomposing point 125°), are obtained by bringing together concentrated aqueous solutions of the corresponding hydrochloride and sodium nitrite. In the case of readily soluble nitrites, comparatively stable nitrite solutions can be obtained. Of aromatic bases, 4-amido-1, 3-xylene which Wallach employed for his examination, forms a solid nitrite, which at the temperature of the room gradually deliquesces.

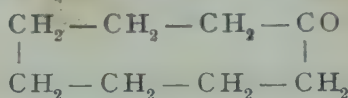
The view which is still largely held, that in converting primary amines with sodium nitrite, the corresponding alcohol must always be formed, does not, according to Wallach, apply, — a fact on which O. Meyer<sup>2)</sup> and M. Freund<sup>3)</sup> have also laid stress. On the contrary, there occur as reaction-products, in addition to hydrocarbon, one or more alcohols isomeric with each other. The direction in which the reaction chiefly progresses depends upon the bases employed and the conditions of the experiment. For instance, l-menthylamine nitrite yields

<sup>1)</sup> Liebig's Annalen **353** (1907), 318.

<sup>2)</sup> Berl. Berichte **9** (1876), 535.

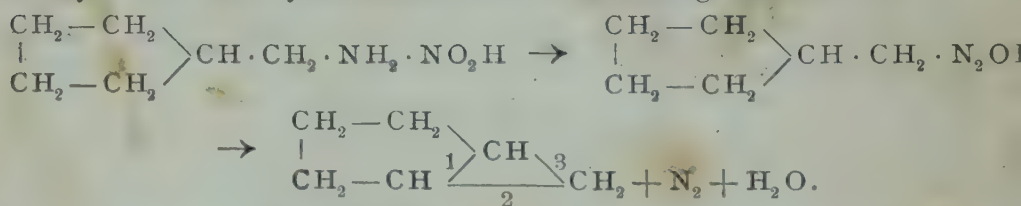
<sup>3)</sup> Ibidem **23** (1890), 2865; **24** (1891), 2150, 3350.

fairly well menthol, d-menthylamine nitrite chiefly menthene. For this reason the study of the cyclyl methylamines obtained from the cyclyl acetic acids<sup>1)</sup> according to well-known methods, was of interest. The examination showed that the nitrites of these bases can be boiled practically without decomposition in neutral aqueous solution, and that by acidifying with acetic acid, there is formed, in addition to hydrocarbons and the corresponding alcohols, an alcohol of the next higher ring-system, which can be oxidised to the corresponding ketone. In this manner the author succeeded in converting cyclopentylamine into cyclohexanone, cyclohexylmethylamine into cycloheptanone (suberone), and cycloheptylmethylamine into cyclooctanone (azelain ketone). The last-named body, which has not yet been described and which has an odour somewhat like oil of bitter almonds,

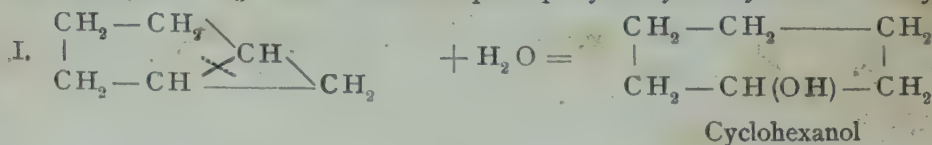


has the following properties: m. p. 25 to 26°; b. p. 195 to 197°<sub>d20°</sub> 0.9581;  $n_D^{20}$  1.4694; m. p. of the semicarbazone 163 to 164.5°.

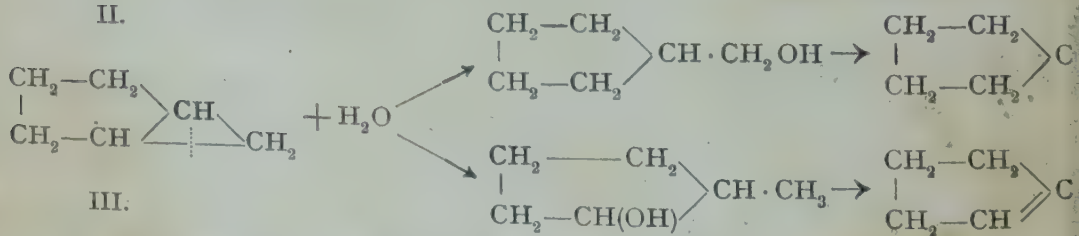
Wallach explains the conversion, for example, of cyclopentylmethylamine into cyclohexanol, in the following manner: —



The tricyclic ring formed can be split up hydrolytically in three ways: —



II.



In formulæ II and III, where the tricyclic ring is assumed to be split up at linking 2 or 3, the secondary products formed on decomposition of the nitrites, a primary and secondary alcohol of the same ring system, and also the corresponding hydrocarbons, are reproduced.

<sup>1)</sup> Comp. the present Report p. 173.







